

Short Communication

Ion conductivity of polymer electrolytes derived from poly(*p*-phenylene terephthalamide)

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Abstract

Polymer electrolytes that exhibit lithium-ion conductivity of the order of 10^{-3} S cm⁻¹ and excellent mechanical strength are prepared by impregnating aqueous gel films of poly(*p*-phenylene terephthalamide) (PPTA) with polyethylene glycol (PEG), polycarbonate in propylene carbonate (polyC·PC), or ethylene carbonate (EC), removing water, and soaking the impregnated polymer in lithium salt solution. The lithium-ion conductivity of the PPTA/PEG systems increases rapidly with the concentration of the LiBF₄ in the lithium salt solution LiBF₄/PC:EC:BL (25:25:50), to a maximum of 2.2×10^{-3} S cm⁻¹ at 0.8 M LiBF₄, then decreases gradually between 1 and 2 M. This suggests that the ion conductivity is the result of LiBF₄ uptake at the amide bond sites of the PPTA. With LiPF₆/PC:EC:BL (25:25:50) in the range 0.8 to 1.5 M LiPF₆, the PPTA/PEG systems exhibit a similar high conductivity. The PPTA/polyC·PC and the PPTA/EC systems also display high lithium-ion conductivities with the LiBF₄ solutions.

Keywords: Ion conductivity; Polymer electrolytes; Lithium-ion batteries

1. Introduction

Practical conductivities of about 10^{-3} S cm⁻¹ at room temperature have been obtained in various polymer electrolyte systems based on host polymers such as poly(vinyl chloride), poly(acrylonitrile) (PAN), and poly(vinylidene fluoride-co-hexafluoropropylene) plasticized by liquid solvents [1–4].

In the work discussed here, a spongy polymer network of poly(*p*-phenylene terephthalamide) (PPTA) in the form of an aqueous gel film is used as the host polymer. It is inherently insoluble in aprotic solvents such as polycarbonate (PC), ethylene carbonate (EC), and γ -butyrolactone (BL). The impregnating materials poly(ethylene glycol) (PEG), polycarbonate in propylene carbonate (polyC·PC), and EC were selected to provide high conductivity rather than for their compatibility with the host polymer. The PPTA gel film was impregnated in the wet state (i.e. solvents thus replaced water in the gel film), as impregnation of the dried film was impracticable by normal impregnation methods. The polymer electrolyte was obtained by soaking the impregnated film in a liquid electrolyte that consisted of LiBF₄ or LiPF₆ in a mixed solvent. It exhibited excellent mechanical strength, attributable to its PPTA network, and high conductivity, attributable

to the conductivity of the liquid electrolyte and the impregnated PPTA film. The ion-conducting behaviour of these PPTA-based polymer electrolytes is described in this communication.

2. Experimental

Wet gel films were made by casting PPTA-doped sulfuric acid solution onto a flat plate and washing it with de-ionized water, as described in Ref. [5]. The average thickness of the films was 29 μ m. Their composition was typically 19 vol.% PPTA and 81 vol.% water. PEG of various molecular weights, PC and EC were reagent grade from Wako Pure Chemical. Low molecular weight polycarbonates (polyC) were obtained from an Asahi Chemical laboratory.

All liquid electrolytes and the mixed solvent PC:EC:BL (25:25:50 by volume) were obtained from Tomiyama Pure Chemical Industry and used as received, with a guaranteed water content of less than 20 ppm. In the impregnation process, the wet gel film was immersed in PEG, polyC·PC, or EC for 10 min at 110 °C, wiped with a cloth containing the mixed solvents after removal and cooling, and then soaked in liquid electrolyte for 5 min under a dry argon atmosphere. The soaked films were transparent, and light yellow in colour.

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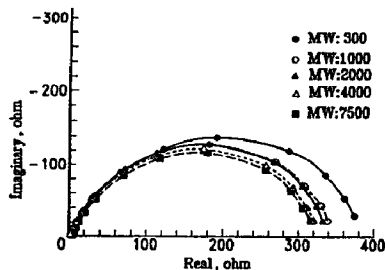


Fig. 1. Cole–Cole plots of PPTA-based polymer electrolytes prepared by impregnation of PEG of several mol. wt. followed by soaking in 1.5 M $\text{LiBF}_4/\text{PC:EC:BL}$ (25:25:50 by volume).

The lithium and boron contents of the PPTA-based polymer electrolyte were determined by boiling a sample of the film in 20 ml of 3 wt.% hydrochloric acid solution for 10 min, adjusting the solution volume to 25 ml, and measuring its lithium content by atomic absorption spectrometry and its boron content by inductively coupled plasma-atomic emission spectroscopy. The content of LiBF_4 per unit volume of the polymer electrolyte was calculated from the lithium content as measured by atomic adsorption spectroscopy and the measured size and weight of the film sample.

Total conductivity (taken as ion conductivity in all except the preliminary investigation) was measured by the standard a.c. impedance method with a frequency range from 20 Hz to 1 MHz using a Hewlett-Packard 4284A precision LCR meter. Two parallel copper discs (10 mm in diameter and 0.5 mm in thickness) were used as the electrodes. The complex impedance of the polymer electrolyte for Cole–Cole plots (Fig. 1) was measured by the a.c. two-terminal method, using the same LCR meter; the electrodes consisted of the same copper discs covered with freshly scraped lithium metal foil and with a 10 mV signal applied across the sample. The electronic conductivity was measured by the two-terminal method with a voltage of 100 mV and d.c., using an Advantest R8340A ultra-high resistance meter with a d.c. voltage source between the copper disc electrodes. The ion conductivity of the liquid electrolytes and the solvent mixture was measured with a Toa Denpa CM20S conductivity meter. All soaking and conductivity measurements were performed at 25 °C. Measurement samples were packed in small polyethylene bags to prevent solvent evaporation, and were handled in a glove box in an argon gas flow to avoid excessive moisture adsorption.

3. Results and discussion

3.1. Preliminary investigation of ion and electronic conductivities

Copper electrodes are commonly employed in rechargeable lithium-ion batteries; they were employed in this study rather than the stainless-steel electrodes that are conventionally used in measurements of electric conductivity. Prelimi-

nary investigation showed the copper electrodes to be appropriate for this purpose. With the copper electrodes, PPTA-based polymer electrolyte prepared by impregnating PEG (average mol. wt. 2000) and soaking in 1.5 M $\text{LiBF}_4/\text{PC:EC:BL}$ solution exhibited an electronic conductivity of $8.3 \times 10^{-3} \text{ S cm}^{-1}$ and a total conductivity of $1.2 \times 10^{-9} \text{ S cm}^{-1}$. With the same electrodes, the total conductivity of a PPTA-based film prepared in the same manner, but with the mixed solvent containing no lithium salt, was $1.0 \times 10^{-7} \text{ S cm}^{-1}$. These results showed that the electronic conductivity with the PPTA-based polymer electrolyte was negligibly small compared with the ion conductivity. Therefore, the total conductivity was taken as representing ion conductivity throughout the remainder of this investigation.

3.2. PEG molecular weight

Polymer electrolytes were prepared with PEG of five mol. wt. in the range 300 to 7500, and their ion conductivities were measured. The mol. wt. of the impregnated PEG had no significant effect on ion conductivity measured at 500 KHz, as shown in Table 1, but clearly influenced the Cole–Cole plots obtained with the lithium-covered electrodes. It may be noted that impregnation with PEG of mol. wt. 2000 or higher resulted in a surface haze on the PPTA film that consisted of a small amount of residual solidified PEG, prior to wiping with the mixed solvents.

3.3. Temperature dependence of ion conductivity

As shown in Fig. 2, the ion conductivity of the PPTA-based polymer electrolyte obtained with PEG of mol. wt. 2000 and 1.5 M $\text{LiBF}_4/\text{PC:EC:BL}$ (25:25:50) exhibits a nearly linear dependence on temperature in the measured range of -20 to 60 °C, with no discontinuity at the PEG freezing point of approximately 40 °C. The temperature dependence of the polymer electrolyte was much smaller than that of the 1.5 M $\text{LiBF}_4/\text{PC:EC:BL}$ (25:25:50) electrolyte in liquid form, as also shown in Fig. 2.

Table 1

Lithium-ion conductivity of PPTA-based polymer electrolytes impregnated with PEG of different mol. wt., after soaking in 1.5 M $\text{LiBF}_4/\text{PC:EC:BL}$

Mol. wt. of PEG	Thickness of polymer electrolyte (μm)	Ion conductivity (S cm^{-1}) $\times 10^{-3}$
300	32	2.0
1000	31	1.8
2000	32	1.8
2000	17	3.0
2000	7	1.0
4000	32	2.0
7500	32	1.6

Table 2

Lithium-ion conductivity of PPTA-based polymer electrolytes impregnated with ethylene carbonate (EC) or with polycarbonate in propylene carbonate (polyC·PC), after soaking in 1.5 M LiBF₄/PC:EC:BL

Impregnating material	Thickness of polymer electrolyte (μm)	Ion conductivity (S cm ⁻¹) × 10 ⁻³
Ethylene carbonate	30	1.5
20 wt.% polyC (mol. wt.:2000), 80 wt.% PC	31	1.1
20 wt.% polyC (mol. wt.:4100), 80 wt.% PC	33	1.2
30 wt.% polyC (mol. wt.:4100), 70 wt.% PC	33	1.6

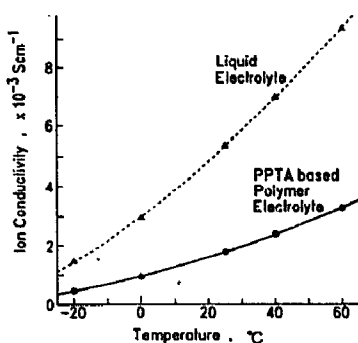


Fig. 2. Temperature dependence of PPTA-based polymer electrolyte prepared with PEG (mol. wt.: 2000) and 1.5 M LiBF₄/PC:EC:BL (25:25:50 by volume).

3.4. Polymer electrolytes with impregnated EC and polyC·PC

The ion conductivities of several PPTA-based polymer electrolytes impregnated with EC or with polyC·PC, instead of PEG, and soaked in 1.5 M LiBF₄/PC:EC:BL (25:25:50) are shown in Table 2. The high ion conductivity obtained with EC impregnation was fully comparable with that obtained with PEG impregnation, and was of particular interest because EC exists as a dry film at room temperature and is therefore easy to handle, and also because EC itself was one of the components of the liquid electrolyte. These characteristics, and the similarity of its Cole–Cole plots to those of the polyethylene separator shown in Fig. 3, indicate that

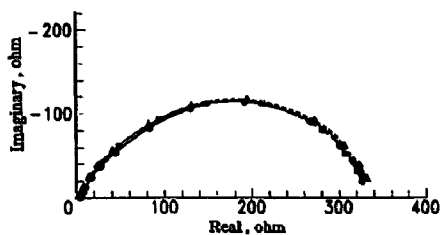


Fig. 3. Cole–Cole plots of two PPTA-based polymer electrolytes and a conventional microporous polyethylene separator. All prepared by soaking in 1.5 M LiBF₄/PC:EC:BL (25:25:50) liquid electrolyte. (●) polymer electrolyte 30 μm thick composed of 13 wt.% PPTA, 48 wt.% EC, 11 wt.% LiBF₄, 28 wt.% PC:EC:BL; (▲) polymer electrolyte 32 μm thick composed of 13 wt.% PPTA, 41 wt.% PEG (MW: 2000), 11 wt.% LiBF₄, 35 wt.% PC:EC:BL; (■) polyethylene separator 35 μm thick soaked with liquid electrolyte.

the PPTA polymer impregnated with EC could be effective as a battery separator, and could be superior in strength and durability to the microporous polyolefin separators currently used for this purpose.

3.5. Lithium salt concentration and ion conductivity

The ion conductivity of the polymer electrolyte was dependent on the concentration of the lithium salt solution used in its preparation. As shown in Fig. 4, the ion conductivity of the PEG-impregnated PPTA polymer electrolyte increased rapidly with the lithium salt concentration in the liquid electrolyte employed for its preparation; the conductivity reached a maximum of 2.2×10^{-3} S cm⁻¹ when prepared with LiBF₄/PC:EC:BL (25:25:50) containing 0.8 to 0.9 M LiBF₄, and gradually decreased with higher LiBF₄ concentrations.

3.6. LiBF₄ in polymer electrolyte

The LiBF₄ content of the above polymer electrolytes (Fig. 4) as calculated from the determination of their lithium content by atomic absorption spectrometry, in relation to the LiBF₄ content of the liquid electrolyte used in their preparation is given in Fig. 5. These results indicate that the PPTA-based film takes up significantly more LiBF₄ than would be expected by a simple filling of its PPTA polymer interstices or voids by the liquid electrolyte, when prepared with liquid

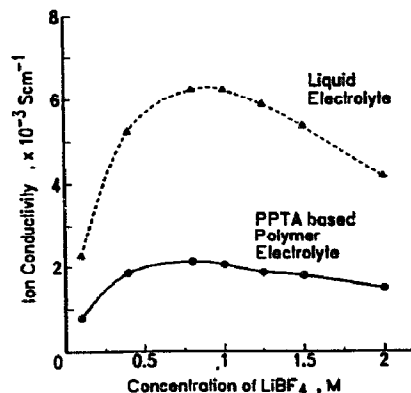


Fig. 4. Ion conductivities of PPTA-based polymer electrolyte and liquid electrolyte vs. LiBF₄ concentration of liquid electrolyte used in soaking.

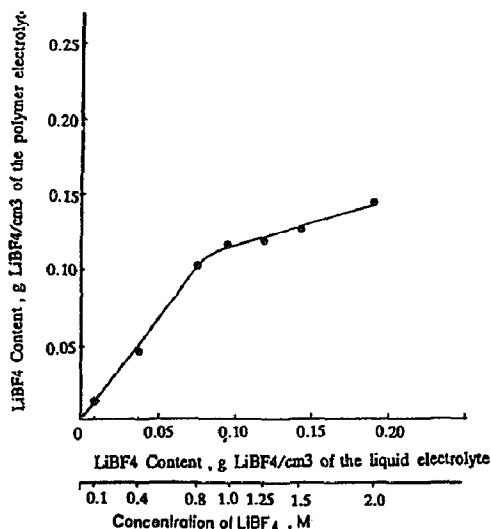


Fig. 5. LiBF₄ content of the PPTA-based polymer electrolyte and the liquid electrolyte used in soaking.

electrolytes that contain 0.1 to 1.5 M LiBF₄, and thus suggests that LiBF₄ is adsorbed by the polymer under these conditions.

Four of the PPTA-based polymer electrolytes, prepared with either PEG or EC and LiBF₄/PC:EC:BL (25:25:50) containing either 1.0 or 1.5 M LiBF₄, were analysed for both their lithium and boron contents, by atomic absorption spectrometry and atomic emission spectroscopy, respectively. As shown in Table 3, the ratio of the lithium and boron contents by weight was consistently 0.7, which is near the ratio of their atomic weights (0.64). This verifies the above calculation of the LiBF₄ content in the polymer electrolyte from its measured lithium content.

The infrared spectra shown in Fig. 6 also support the inference of LiBF₄ adsorption by the polymer. In the spectrum of the PPTA-based film, impregnated with PEG and soaked in PC:EC:BL containing no LiBF₄, the PEG and the amide peaks are visible at 1120 and 3524 cm⁻¹, respectively. In the spectrum of the polymer electrolyte, prepared in the same way but with 1.5 M LiBF₄ present in the soaking solution, the PEG peak remains at the same location but the amide peak is shifted by about 39 cm⁻¹, (to 3564 cm⁻¹) and this implies some type of interaction between the amide and the LiBF₄. One scheme of interaction which might be considered is the following, in which the Li salt-solvate (I), formed when the Li salt (LiBF₄) is dissolved in the PC/EC/BL solvent mixture, is desolvated in the PPTA polymer network

Table 3
Analyses of lithium and boron in PPTA-based polymer electrolyte

LiBF ₄ concentration of liquid electrolyte at soaking (M)	Impregnated material	Lithium content (wt.%)	Boron content (wt.%)	Calculated ratio of Li/B
1.0	PEG (mol. wt.:2000)	0.6	0.8	0.7
1.5	PEG (mol. wt.:2000)	0.8	1.1	0.7
1.0	EC	0.6	0.8	0.7
1.5	EC	0.8	1.1	0.7

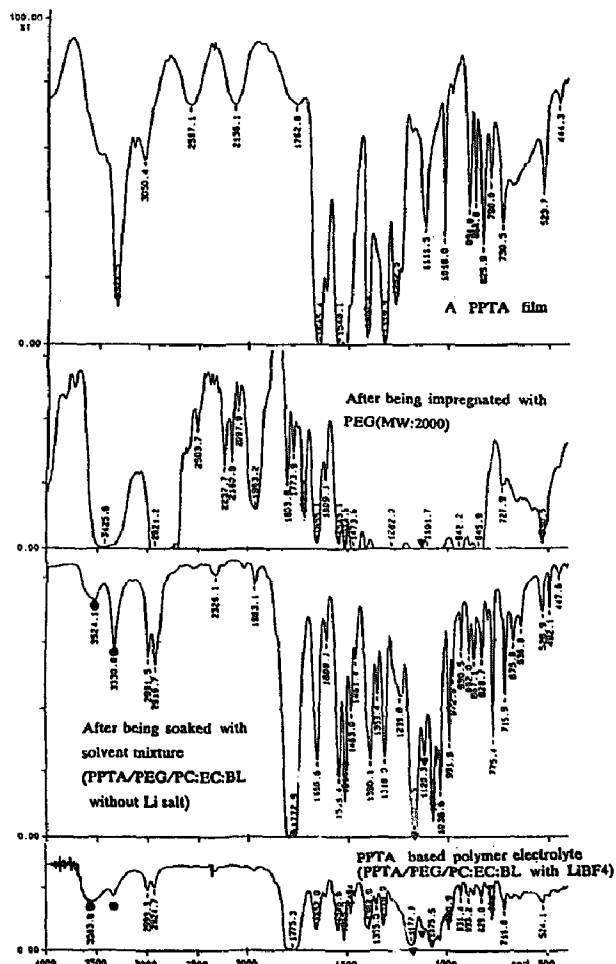
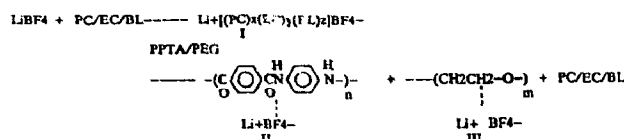


Fig. 6. Infrared spectra of PPTA film before and after impregnation with PEG and soaking in LiBF₄/PC:EC:BL.

by electrostatic forces between the lithium salt and the polymer (II) and also between the Li salt and PEG (III).



3.7. Conductivity with LiPF₆

A similar high ion conductivity was obtained with polymer electrolytes prepared with LiPF₆ instead of LiBF₄, as shown

Table 4
Ion conductivity of PPTA-based polymer electrolytes prepared with LiPF_6 , by soaking in $\text{LiPF}_6/\text{PC}:\text{EC}:\text{BL}$ of several concentrations after impregnation with PEG (mol. wt. 2000)

LiPF_6 concentration in liquid electrolyte (M)	Thickness of polymer electrolyte (μm)	Ion conductivity (S cm^{-1}) $\times 10^{-3}$
0.8	24	2.0
1.0	24	2.1
1.25	22	1.6
1.5	20	1.3

in Table 4. Among the polymer electrolytes prepared with $\text{LiPF}_6/\text{PC}:\text{EC}:\text{BL}$ (25:25:50) containing LiPF_6 in concentrations of 0.8 to 1.5 M, the electrolyte prepared with 1.0 M LiPF_6 exhibited the highest ion conductivity of $2.1 \times 10^{-3} \text{ S cm}^{-1}$. Further studies on this PPTA-based polymer electrolyte and its application in rechargeable lithium-ion batteries are now in progress.

4. Conclusions

PPTA-based polymer electrolytes, prepared by impregnating wet gel films of PPTA with PEG, EC, or polyC·PC,

followed by soaking in the solvent mixture PC:EC:BL (25:25:50) containing LiBF_4 or LiPF_6 , exhibit lithium-ion conductivity of the order of $10^{-3} \text{ S cm}^{-1}$. Adsorption of the lithium salt by the PPTA polymer is suggested by the high content of lithium found in the PPTA polymer electrolytes.

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