

Conductive behaviour of lithium ions in polyacrylonitrile

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Abstract

The conductivity of lithium ions in polyacrylonitrile (PAN) is examined. Using the d.c. polarization method, the electric transport coefficient was observed to be less than 0.05. X-ray diffraction analysis confirms that PAN-LiClO₄ has an amorphous structure. Fourier-transform infrared spectroscopy results indicate that Li⁺ ions form bonds not only with the C≡N groups of the PAN, but also with C=O groups of the dimethylformamide. The relationship between conductivity and temperature suggests that the conduction of Li⁺ ions in PAN is achieved through the polymer backbone's segmental motion. Finally, the activation energy of PAN(LiClO₄)_{0.2} is estimated to be 86 kJ/mol.

Keywords: Lithium batteries; Solid polymer electrolytes; Conductivity

1. Introduction

The conductive behaviour of lithium ions in solid polymer electrolytes (SPE) has received increasing interest [1–24]. Reich and Michaeli [14] have examined the conductivity of systems formed by adding LiClO₄ to polyacrylonitrile (PAN). Watanabe et al. [11] used ethylene carbonate (EC) or propylene carbonate (PC) as a plasticizer for LiClO₄ complexes of PAN, and also measured the conductivity of the dry membrane. Also, Tsuchida et al. [15] demonstrated that conductivity does not depend on the concentration of the salt, but rather on the ratio of plasticizer to salt. The conductivity of PAN is about 10⁻⁷–10⁻⁸ S cm⁻¹ if EC:Li⁺ = 0.5. If the ratio is 2, the conductivity is around 10⁻⁴–10⁻⁵ S cm⁻¹. Tsunemi et al. [16] also found that the conductivity changes slightly if the amount of salt in PAN is changed. By contrast, the concentration of the salt in plasticizers affects markedly the ionic conductivity. Abraham and Alamgir [1] increased the conductivity to 10⁻³ S cm⁻¹ by adding PC and ethylene carbonate (EC) to PAN. Nevertheless, the role of residual organic solvent in PAN has remained unclear. This study examines the conductive behaviour of lithium ions in PAN, together with the relationship between lithium ions and the residual organic solvent. The effects of contact pressure and temperature between the electrodes and PAN are also investigated.

2. Experimental

2.1. Preparation of SPE

LiClO₄ (Stream Chemicals) was first dissolved in dimethylformamide (DMF) (Fisher Scientific Chemicals) with the solution heated at a designated temperature. After completely dissolution, PAN (Polyscience Chemicals, mol. wt. = 150 000) was gently poured into the solution, followed by continuous stirring. Next, the conductivity of the solution was measured with a conductivity meter (WTW LF539). The DMF residue in the SPE membrane was estimated to be less than 4.5 wt.%.

2.2. X-ray diffraction analysis

An X-ray diffractometer (XRD) (Shimadzu XD-5) was used to analyse the structures of LiClO₄, PAN, and PAN-LiClO₄. Diffraction angles were measured in the range: 10° to 60°.

2.3. Measurement of SPE conductivity

The measuring system is shown in Fig. 1. Fig. 1(a) and (c) gives cross-sectional views of two cylinder-type parts that are assembled together and placed in position 5 of Fig. 1(b). The working and counter electrodes were polished platinum plates and were placed at positions 1 and 2. The electrodes and the membrane electrolyte were assembled as a sandwich and were inserted into (A) and adequately cov-

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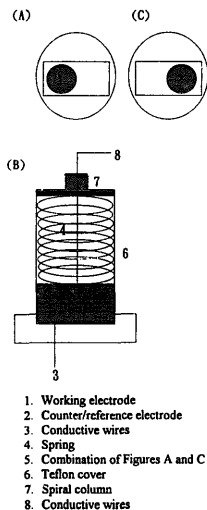


Fig. 1. System for conductivity measurements.

ered with (C) ((A) and (C) are made of Teflon), and then placed at position 5. Optimal contact pressures between the electrodes and electrolyte were obtained and controlled by the pressure applied towards the spiral column and the spring. Membranes (thickness: $30\ \mu\text{m}$) were cut into $1\ \text{cm}^2$ squares. The square sample was placed on top of the working electrode and then covered with the counter electrode in a sandwiched form. Next, conductive wires were connected to an a.c. impedance analyser (Eco Chemie Autolab). Impedance spectra were recorded over the frequency range $50\ \text{kHz}$ to $1\ \text{Hz}$. The voltage amplitude was $10\ \text{mV}$.

The measurement system was placed in a heating chamber. The temperature was set at 25, 35, 55, 65 and $95\ ^\circ\text{C}$, respectively, for 2 h. After the temperature reached equilibrium, the impedance of the SPE was measured.

2.4. D.c. polarization measurement

The transport number of an electrolyte is an important index of its conductive behaviour. In this study, d.c. polarization is used to measure the transport number. A sample plate of PAN– LiClO_4 was placed at position 1, as shown in Fig. 1. A fixed voltage of $250\ \text{mV}$ was applied with a potentiostat. The correlation between current and time was recorded until the current reached a steady state.

2.5. FT-IR measurement

Functional groups of PAN, PAN– $(\text{LiClO}_4)_{0.1}$, and PAN– $(\text{LiClO}_4)_{0.15}$ were studied by Fourier-transform infrared

spectroscopy (FT-IR) (Bomem DA 3.002) with wavenumbers in the range from 2300 to $550\ \text{cm}^{-1}$. It should be possible to elucidate the bonding of lithium ions to the polymer as well as its effect on the mechanism of conductivity.

3. Results and discussion

3.1. Conductive behaviour of lithium ions in PAN

XRD patterns for LiClO_4 are shown in Fig. 2(a). The diffraction peaks indicate the crystalline phase of LiClO_4 . Fig. 2(b) summarizes the PAN results; no diffraction peak appears since PAN is amorphous. The pattern for PAN– LiClO_4 is given in Fig. 2(c) and is similar to that shown in Fig. 2(b). This means that the SPE of PAN– LiClO_4 remains amorphous after LiClO_4 is added. Previous work has indicated [20] that ionic pairs would exist and a crystalline phase should be detected when salt is added to the polymer. Nevertheless, ionic pairs could not be found in the system examined here. Ratner [21] found the ionic conduction of SPE to occur primarily with the non-crystalline phase. Therefore, the SPE of PAN– LiClO_4 should be a very good ionic conductor.

When a PAN– $(\text{LiClO}_4)_{0.15}$ membrane was under a constant voltage of $250\ \text{mV}$, the current varied with time as shown in Fig. 3. Using the Watanabe et al. [22] method, the electronic transport coefficient of PAN– $(\text{LiClO}_4)_{0.15}$ was found to be 0.05. This value confirms that the conduction of an SPE of PAN– LiClO_4 is achieved primarily through movement of the ions.

The change in impedance of a PAN– LiClO_4 membrane under different pressures is presented in Fig. 4. As the pressure is increased, the impedance of the electrolyte decreases and finally levels off. This observation suggests that contact between electrodes and electrolyte is a critical factor when measuring the conductivity of an SPE. With an insufficient amount of pressure, the resistance becomes very large. On the other hand, the structure of the SPE would be destroyed

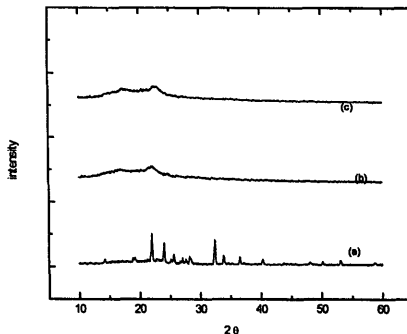


Fig. 2. XRD analysis of: (a) LiClO_4 ; (b) PAN, and (c) PAN– LiClO_4 .

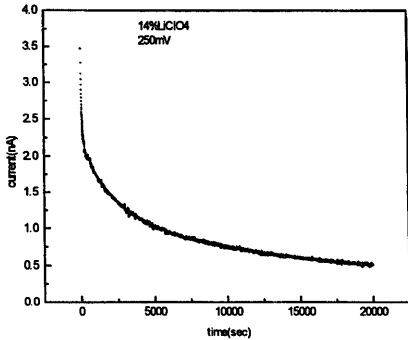


Fig. 3. Current vs. time at a constant voltage of 250 mV.

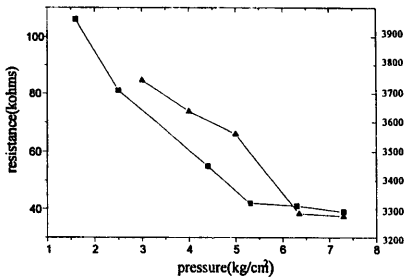


Fig. 4. Relationship between impedance and pressure at electrodes: (■) smooth surface, and (▲) wrinkled surface.

Table 1
Conductivity of a solid polymer electrolyte (SPE) that comprises PAN with different LiClO₄ concentrations

SPE	Conductivity (S cm ⁻¹)
PAN-(LiClO ₄) _{0.01}	< 10 ⁻¹¹
PAN-(LiClO ₄) _{0.05}	< 10 ⁻¹¹
PAN-(LiClO ₄) _{0.1}	1.36 × 10 ⁻⁹
PAN-(LiClO ₄) _{0.20}	6.51 × 10 ⁻⁷
PAN-(LiClO ₄) _{0.25}	6.22 × 10 ⁻⁸

[24], if the pressure of contact is too large. The optimum contact between electrode and electrolyte can be reached by adjusting the spring (see Fig. 1). In addition, the evenness of the SPE also affects the electrode–electrolyte contact area. More pressure is required to reach a stable impedance value if the SPE's surface is less smooth, see Fig. 4(b). Table 1 lists the conductivities of PAN–LiClO₄ with different LiClO₄ contents. The impedance becomes extremely large if the concentration is between 1 and 5 wt.%; the estimated conductivity is less than 10⁻¹¹ S cm⁻¹. As the LiClO₄ concentration reaches 20 wt.%, the conductivity increases to 10⁻⁷ S cm⁻¹

due to the fact that more carrier ions are present. The conductivity drops to 10⁻⁸ S cm⁻¹, however, when the concentration is raised to 25 wt.%. It is plausible that a high ion concentration leads to stronger ion–ion interaction and, thereby, possibly impedes the polymer backbone's segmental motion and ultimately causes a lowering of the conductivity. Because of these two effects, there must be an optimal concentration of LiClO₄. A similar result is obtained when LiClO₄ is added to polyethylene oxide (PEO) or polypropylene oxide (PPO) [20].

The effect of temperature on the conductivity of various electrolytes is shown in Fig. 5. The conductivity of LiClO₄/DMF varies only slightly as the temperature is increased. By contrast, the conductivity of an SPE of PAN–LiClO₄ increases markedly with rise in temperature (Fig. 5(a), (b)). This implies that the conductivity increase does not originate from the SPE's residual organic solvent, but is due to the polymer backbone's segmental motion. Previous studies [9,16–18,20] have shown that this motion is strongly related to the glass transition temperature (*T_g*). As the temperature approaches the *T_g* of the SPE, the polymer backbone's segmental motion is severe. Thus, the present finding correlates with previous reports.

A linear relationship of log σ versus 1/*T* is shown by the data presented in Fig. 5. Such a relationship can be understood in terms of the Arrhenius equation

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (1)$$

where σ_0 is the conductivity factor and *E_a* is the activation energy. The activation energy of PAN–(LiClO₄)_{0.2} was found to be 86 kJ/mol.

The Nyquist plot of PAN–(LiClO₄)_{0.2} electrolyte at various temperatures is given in Fig. 6. Clearly, the left semicircles gradually fade away when the temperature is raised. Generally, the conductivity of a fluid lithium electrolyte is better (greater than 10⁻³ S cm⁻¹) than SPE. For a fluid electrolyte system, only the resistance effect can be found;

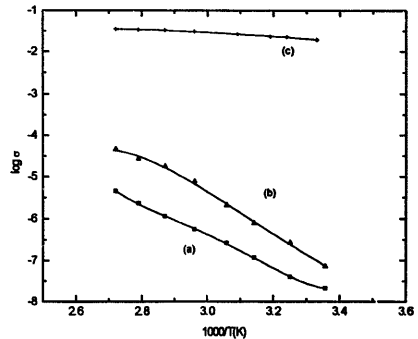


Fig. 5. Relationship between specific conductivity (σ) and temperature: (a) PAN–(LiClO₄)_{0.15}; (b) PAN–(LiClO₄)_{0.2}; and (c) 1 M LiClO₄/DMF.

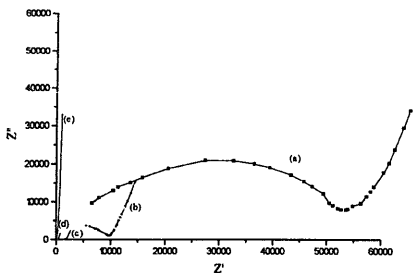


Fig. 6. Nyquist plot of PAN-(LiClO₄)_{0.2} at (a) 25, (b) 35, (c) 55, (d) 65, and (e) 95 °C.

this originates from the electrolyte's bulk solution. In this case, ions respond quickly as the electric potential alternates between positive and negative in an a.c. electric field. Notably, ions are not stagnant during conduction. Therefore, no capacitance effect would occur. On the other hand, for an SPE system, the capacitance effect would occur due to the delayed motion of ions. In a Nyquist plot, semicircles denote the capacitance effect. As shown in Fig. 6, a rise in temperature causes the capacitance effect to be curtailed. This result indicates that the polymer backbone's segmental motion becomes severe as the temperature rises, which further increases the ionic conductivity. This occurrence corresponds to the results given in Fig. 5.

3.2. Bonding of lithium ions with PAN and DMF

Although previous results indicate that the residual solvent clearly has little influence on the conductivity of the electrolyte, its interaction with the polymer still deserves further study.

The FT-IR spectra for PAN, PAN-(LiClO₄)_{0.1}, PAN-(LiClO₄)_{0.15}, and PAN-(LiClO₄)_{0.2} membranes are shown

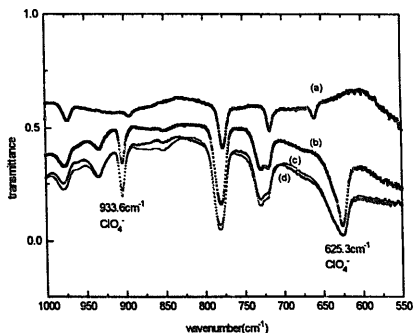


Fig. 7. FT-IR spectra from 1000 to 550 cm⁻¹: (a) PAN; (b) PAN-(LiClO₄)_{0.1}; (c) PAN-(LiClO₄)_{0.15}, and (d) PAN-(LiClO₄)_{0.2}.

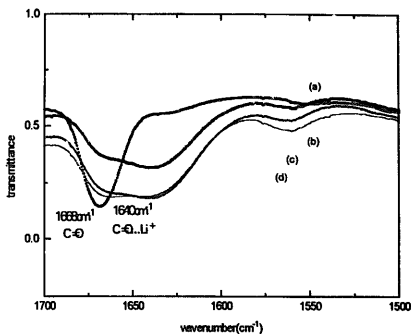


Fig. 8. FT-IR spectra from 1700 to 1500 cm⁻¹: (a) PAN; (b) PAN-(LiClO₄)_{0.1}; (c) PAN-(LiClO₄)_{0.15}, and (d) PAN-(LiClO₄)_{0.2}.

in Fig. 7–9. In Fig. 7, the wavenumbers of 625 and 933.6 cm⁻¹ are the absorption peaks of ClO₄⁻ [25–27]. A rise in the LiClO₄ concentration causes the ClO₄⁻ concentration to increase as well. In Fig. 8, the absorption peak of PAN at 1668 cm⁻¹ is the peak of C=O for the residual solvent DMF. For PAN-LiClO₄ membrane, the peak becomes much wider from 1580 to 1690 cm⁻¹ in Fig. 8. Obviously there are two overlapping peaks (1640 and 1668 cm⁻¹) in Fig. 8. It is considered that this widening occurs since Li⁺ bonds with C=O and, thereby, enables the C=O peak to move from 1668 to 1640 cm⁻¹. Because a portion of C=O remains unbonded with Li⁺, the peak at 1668 cm⁻¹ still exists. The peak at 2243 cm⁻¹ in Fig. 9 represents the functional group of C≡N in PAN. When LiClO₄ is added, a peak at 2269 cm⁻¹ appeared on the left-hand side. This is a displacement peak due to the interaction between Li⁺ and C≡N. Since not all of the C≡N bonds interact with Li⁺, the peak at 2243 cm⁻¹ is still present. These results indicate that when Li⁺ bonds with oxygen, electrons move from oxygen to the lithium ions,

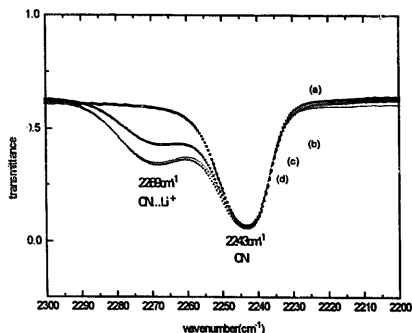


Fig. 9. FT-IR spectra from 2300 to 2200 cm⁻¹: (a) PAN; (b) PAN-(LiClO₄)_{0.1}; (c) PAN-(LiClO₄)_{0.15}, and (d) PAN-(LiClO₄)_{0.2}.

and, accordingly, weaken the bonding strength between carbon and oxygen. Moreover, as C=O combines with lithium ions, the absorption peak shifts towards a lower wavenumber. This behaviour is similar to the situation in which acetone is added to LiClO_4 or AgClO_4 , and the absorption peak of C=O shifts towards a lower wavenumber [28].

For C≡N bonds, however, carbon and nitrogen are conjugated with a triple bond and double bond [29]. Hence, C≡N is not exactly the same as C=O. Adding a compound capable of bonding with C≡N causes the conjugated bond to disappear. The carbon and nitrogen thereby only exist as a triple bond. In addition, the bonding strength increases. Peaks at high wavenumbers would subsequently appear [28,29]. This reasoning corresponds to the results found in this system. Thus, a bonding between C≡N and Li^+ in the system examined here has been confirmed.

4. Conclusions

The following conclusions have been reached.

1. The contact resistance of the electrode–electrolyte interface can affect greatly the measurement of an SPE's conductivity. A proper control of the contact pressure of the electrode–electrolyte interface is essential for accurate measurement of the conductivity.

2. PAN– LiClO_4 is an amorphous electrolyte. Its electron transport coefficient is less than 0.05. This implies that PAN is a good ionic conductor.

3. FT-IR information indicates that Li^+ ions bond with C≡N in PAN, and a portion of Li^+ ions bond with C=O from the residual solvent DMF.

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