The characteristics of polymer electrolyte for lithium polymer battery

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Abstract

A lithium ion battery with polymer electrolyte is expected as a safe and long cycle life battery. This paper reports primarily the recent development results of a solid polymer electrolyte, which is a key factor of the secondary battery system, that has been obtained during the process of the development of a polymer type lithium battery. As a successful result of the solid polymer electrolyte. The ionic conductivity of the solid polymer electrolyte, which is composed of polyacrylonitrile and $LiClO_4$ with Al_2O_3 dissolved as the supporting electrolyte, has been confirmed to be 2.3×10^{-4} S/cm at room temperature.

초 록 : 리튬이차전지는 충방전의 반복 동안의 액체전해질과 리튬음극과의 반응으로 수지상결정의 성장으로 리튬이 차전지에 있어서 안전성의 문제를 일으킨다. 고분자 전해질은 수지상 결정 형성을 억제하며 전해질에 성능을 향상시키는 연구가 활발히 진행중이다. 본 연구에서는 겔 전해질에 Al_2O_3를 첨가하여 전해질의 표면구조와 임피던스 특성을 조사하였다. 리튬이온의 수율은 10 wt% PAN-Al_2O_3 전해질에 5 mV의 전압을 인가했을 때 0.29였고 전해질의 이온전도도는 상온에서 2.3×10^{-4} S/cm 였다. 무기 충진제가 고분자 전해질에 첨가되었을 때 이온전도도 및 이온수율은 무기 충진제가 첨가되지 않은 것보다 높게 나타났다.

Key words : Polymer electrolyte, Polymer cathode, Lithium polymer battery

1. Introduction

Lithium rechargeable batteries based on solid polymer electrolyte technologies are now been proposed for a wide variety of extremely demanding applications such as electric vehicle (EV), start-light-ignition (SLI), and portable electronic and personal communication. Lithium polymer electrolyte technology has been recognized as a highly flexible and versatile technological approach for the production of high energy density batteries. It is unlikely that a single lithium polymer electrolyte rechargeable battery technology will be capable of meeting all of the application specific performance parameters which are common to all lithium polymer electrolyte battery technologies and which will be required to ensure technological success in any application.[1,3]

Solid electrolyte must function as both a separator and an electrolyte in battery, and a number of properties are critical for their successful use in batteries. From an electrochemical point of view, the electrolyte must satisfy a minimum of requirements. They must be electrochemically stable, in a voltage window that is at least as wide as the voltage window defined by the electrode reactions. They must have sufficient conductivity to allow a reasonable current density, which will depend on the intended use of battery. They must be chemically and electrochemically compatible with electrode materials and other components they may be in contact with in the battery, and good thermal stability is also required, especially in contact with the lithium electrode.[5,6,8]

New type of polymer electrolyte is gel-type which obtained by the addition of large quantity of liquid plasticizer and solvent to a polymer matrix capable of forming a stable gel with the polymer host structure. The gel electrolytes were originally described by Feuillade and Perche and were further characterized by Watanabe *et al.*[9] The latter reported that the ionic conductivity of the hybrid film does not correlate with the content of $LiClO_4$ in the polyacrylonitrile (PAN) but with the mole ratio EC : $LiClO_4$ in the films. When the ratio is about 2, the conductivity attains $10^{-4} \sim 10^{-5}$ S/cm at room temperature.[4,7,10]

This work characterizes the electrochemical properties of the polymer electrolyte and examins the effect of Al_2O_3 material in the polymer electrolyte.

2. Experimental

The polymer gel electrolytes were prepared from a solution of 40 wt% EC. 40 wt% PC/10 wt% PAN/10 wt% $LiClO_4$ and 40 wt% EC/40 wt% PC/15 wt% PAN/10 wt% $LiClO_2$. Where noted, Al_2O_3 was added as inorganic filler such as Al_2O_3 powder with average dimeter 1 μm was suspended in this polymer electrolyte to imporve ionic conductivity and yield of lithium, The components were stirred and at

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50°C until completely dispresed, and then the solutions were heated in a glass vial, inside the dry box, to 120°C to obtain a homogeneous solution. The solution was then poured between two stainless steel shims, and rolled into thin membranes. On cooling, dimensionally stable, freestanding electrolyte films with thickness about 450 μm were formed. Using a SUS blocking electrode and Li non-blocking electrode performed the ionic conductivity and lithium ion yield measurement by A.C. impedance method. The measurement was carried out from 65 kHz to 0.1 Hz at room temperature. The apparatus used was the electrochemical interface EG& G 273 and M 5210 frequency response analyzer, which were controlled by computer. Fig. 1 exhibits test system. Scanning electron microscopy (SEM) was performed to observe the morphology of polymer electrolyte and distribution of Al₂O₃ which acts as an improving angent usin Hitachi S-2500C.

3. Results and Discussion

The impedance spectra of a Li/SPE/Li cell at various contents of PAN-Al₂O₃ under open-circuit voltage (OCV) condition at room temperature are given Fig. 2.

The impedance of the cell is composed of the bulk resistance, R_b, of the polymer electrolyte and the interfacial resistance, R_e, which represents the interface situation between the electrode and electrolyte. At high frequency, the line intercepts the real part (Z') and this point corresponds to the bulk resistance of polymer electrolyte.

It can be seen in Fig. 2 that bulk resistance R_b, which respects the ionic conductivity, change very little. The R_e corresponding to the resistance of the interface with lithium grew to about 1.5 times of the initial value. The capacitor component C_e showed no change remaining at about 2.2F.
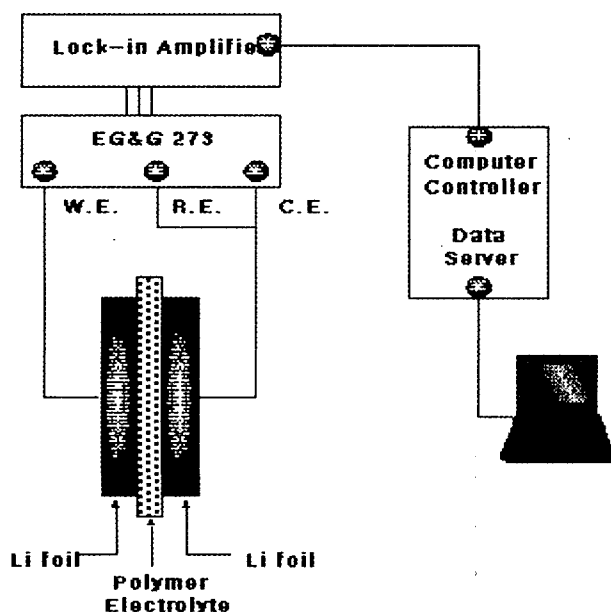

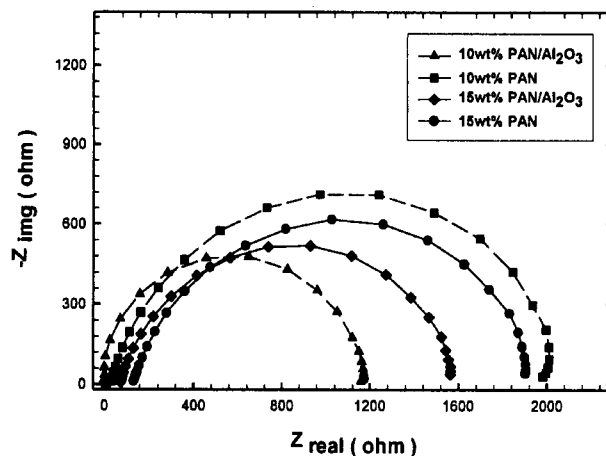Fig. 1. Schmatic diagram of the structure of lithium polymer battery.

Fig. 2. Impedance spectra of Li/15 wt% PAN-EC-PC-LiClO₄/Li cell.

This suggests that inorganic filler decreased the resistance monotonously monotonously.

This allows calculation of the ionic conductivity of the polymer electrolyte with a cell constant value of 0.005 cm⁻¹. The electrolyte maintained a conductivity of 2.3×10⁻⁴ S/cm at room temperature.

The value of interface resistance (R_e) was decreased adding Al₂O₃. This phenomenon can be attributed to the formation of passivation layer due to the reactivity of electrode and electrolyte. The C_{dl}, R_b, R_e and σ(S/cm) was summarized in Table 1.

The interfacial capacitance, C_e, is easily calculated from equation (1). The value is independent of time and reaches value of about 1 F/cm².

$$C_e = \frac{1}{R_e\, \omega_{max}} \tag{1}$$

where ω_{max} is the maximum angular frequency of the semicircle; the magnitude of the resistor and capacitor are equal.

Fig. 3~6 show Nyquist plots of various polymer electrolyte cell as a function of polarization. The yield of lithium ion was measured by DC current applied voltage of -5 mV, 5 mV and 10 mV and then worked AC impedance methode using non-blocking electrode system (Li/SPE/Li). The polarization current with time was decreased. The decrease of polarization current as a function of time seemed due to the polarization of the ClO₄⁻ ion in the polymer electrolyte because the lithium electrode is a non-blocking electrode for Li⁺ ions but a blocking electrode for the anion. The steady state current of polarization was observed for 6 hr.

When DC 5 mV was applied the yield of 15 wt% PAN-Al₂O₃ electrolyte and 15 wt% PAN elctrolyte were 0.26 and

Table 1. Ionic characteristic of various polymer electrolyte

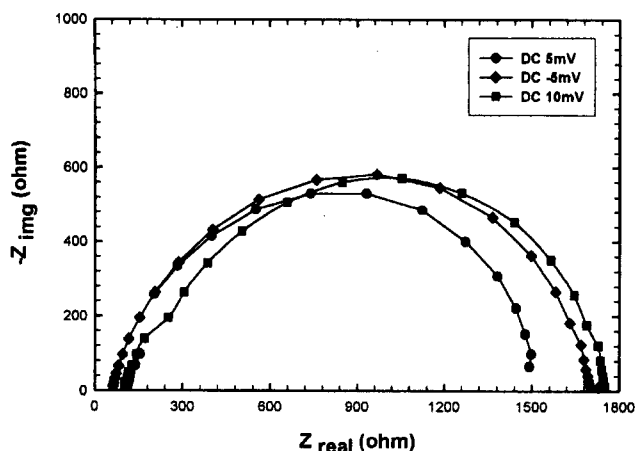| Sample	T (cm)	A (cm²)	R_b (Ω)	C_{dl} (μF)	R_e (Ω)	σ (S/cm)
10 wt% PAN	4.5×10⁻²	4	34	0.51	1947	2.30×10⁻⁴
10 wt% PAN-Al₂O₃	4.5×10⁻²	4	8	2.19	1150	8.92×10⁻⁴
15 wt% PAN	4.5×10⁻²	4	131	0.90	1768	0.57×10⁻⁴
15 wt% PAN-Al₂O₃	4.5×10⁻²	4	74	1.06	1490	1.00×10⁻⁴

Fig. 3. Impedance spectra of Li/15 wt% PAN-Al₂O₃-EC-PC-LiClO₄/Li cell as a function of polarization.
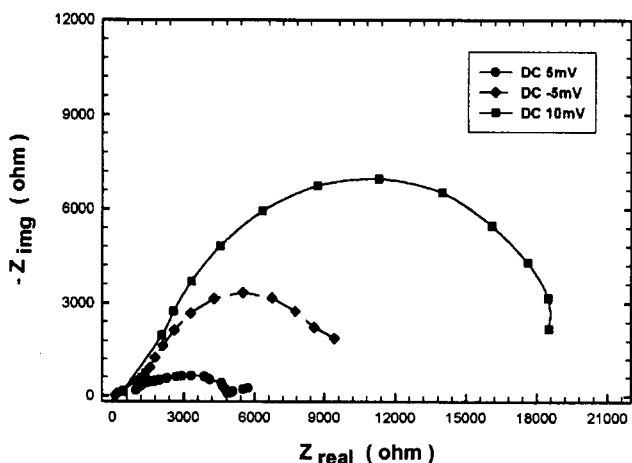

Fig. 4. Impedance spectra of Li/15 wt% PAN-EC-PC-LiClO₄/Li cell as a function of polarization.

0.04, respectively. When DC 5 mV was apllied the yield of 10 wt% PAN-Al₂O₃ electrolyte and 10 wt% PAN electrolyte were 0.29 and 0.05, respectively.

It means that inogranic filler promote polymer segmental motion for ion transport and decrease the interface resistance. Also it was shown that the yield of lithium ion is independent of the content of host polymer and amount of Al₂O₃. The interface resistance of PAN gel electrolytes showed minimum value at DC 5 mV.

The transfer number of SPE electrolyte was measure by polarization method and AC impedance method calculated by equation (2)

$$t_{Li^+} = \frac{R_b}{\left(\dfrac{\triangle V}{I_\infty}\right) - R_e} \qquad (2)$$

where $\triangle V$ is applied voltage, R_b is bulk resistance, R_e is interface resistance, I_∞ is steady state current. The transfer number t_{Li}^+ of SPE electrolyte was shown in Tables 2 and 3.

Nyquist plot of Li/PAN-Al₂O₃/Li cell were made at applied DC voltage of -5 mV, 5 mV and 10 mV, respectively.

Table 2. Characteristic of 15 wt% PAN and 15 wt% PAN/Al₂O₃ polymer electrolyte

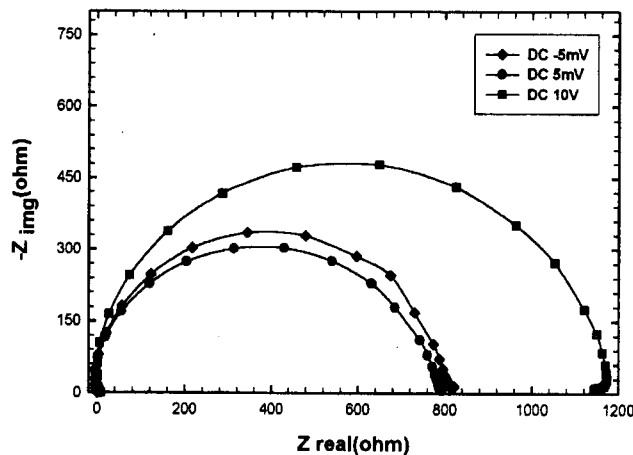|	DC	I_∞ ($\wedge$/cm)	R_b (Ωcm²)	R_e (Ωcm²)	t_{Li}^+
15 wt% PAN	-5 mV	-4.56	132	9418	0.01
	5 mV	5.21	164	4812	0.04
	10 mV	2.98	429	18518	0.02
15 wt% PAN-Al₂O₃	-5 mV	-4.28	62	1728	0.14
	5 mV	5.12	137	1492	0.26
	10 mV	3.11	102	1751	0.06

Fig. 5. Impedance spectra of Li/10 wt% PAN-Al₂O₃-EC-PC-LiClO₄/Li cell as a function of polarization.

When DC 10 mV was applied, the interface resistance of PAN gel electrolyte showed maximum value. The resistance of 15 wt% PAN-Al₂O₃ is much less than that of 15 wt% PAN. Also the resistance of 10 wt% PAN-Al₂O₃ is much less than that of 10 wt% PAN.

Electrochemical impedance spectroscopy at OCV (open circuit voltage) to find effect of each component. Warburg impedance at low frequency showed decreased diffusion resistance with on adding of Al₂O₃. The mobility of lithium ion in polymer electrolyte is dominated by the resistor, R_b, The equivalent circuit of Li/SPE interface is represented by
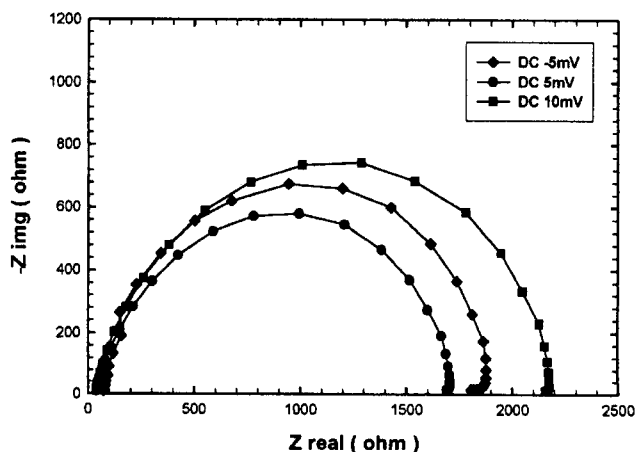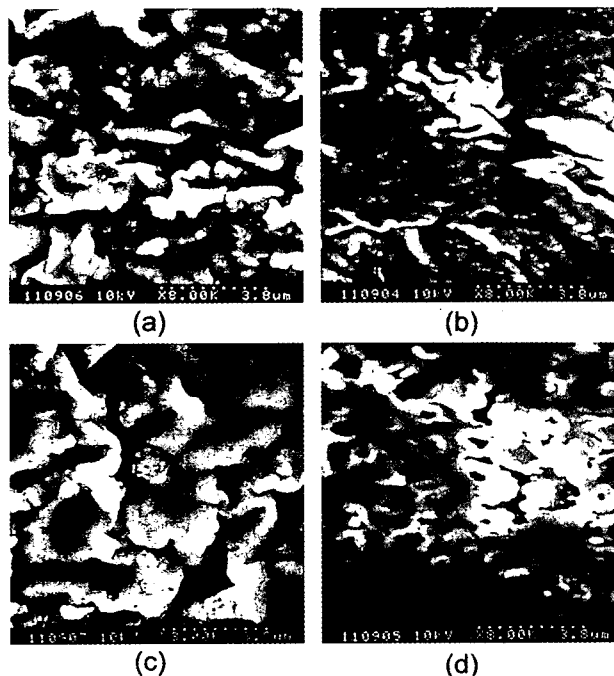

Fig. 6. Impedance spectra of Li/10 wt% PAN-EC-PC-LiClO₄/Li cell as a function of polarization.

Table 3. Characteristic of 10 wt% PAN and 10 wt% PAN/Al₂O₃ polymer electrolyte

	DC	I_∞ (A/cm)	R_b (Ωcm^2)	R_e (Ωcm^2)	t_{Li}^+
10 wt% PAN	-5 mV	-4.90	74	1807	0.09
	5 mV	5.37	40	1691	0.05
	10 mV	3.21	40	2157	0.04
10 wt% PAN-Al₂O₃	-5 mV	-5.88	1	822	0.13
	5 mV	6.14	5	793	0.29
	10 mV	5.88	8	1140	0.01

Fig. 7. SEM photographs of polymer electrolyte. (a) 10 wt% PAN, (b) 10 wt% PAN-Al₂O₃, (c) 15 wt% PAN, (d) 15 wt% PAN-Al₂O₃.

a parallel combination of passivation layer resistance (R_e) and capacitance (C_d).

The AC impedance response of Li/SPE/Li cells exhibited a progressive expansion of DC applied voltage due to passivation layer. The transfer number of SPE was measured by DC polarization methode and AC impedance method described equation. Typically AC impedance of Li/SPE/Li cell consist of a semicircle in the frequency range of 0.1 Hz to 65 kHz. The semicircle represents the charge transfer process and process and polymer electrolyte of passivation layer on the lithium electrode.

The structure and charge transport mechanism for polymer electrolyte differs greatly from those of inorganic solid polymer electrolyte. Ion transport of polymer electrolyte is strongle

dependent of local motion of polymer in the vicinity of the ion polymer structure. The morphology of each polymer electrolyte was shown in Fig. 7. From Fig. 7(b), (d), we observed that distribution of Al₂O₃ into the polymer electrolyte has improved well. It can be concluded that distribution of Al₂O₃ is related to ionic conductivity and lithium ion yield. From Fig. 7(c), (d) we can see above more detailed. Fig. 7(d) was observed little pore, which dispersed into polymer electrolyte. The pores promote the movement of lithium ion moving and ion conductivity.

4. Conclusion

In the PAN SPE gel polymer electrolyte, adding some Al₂O₃, interface resistance was decreased. It means that polymer electrolyte which adding Al₂O₃ is softening polymer electrolyte. When inorganic filler was added into polyacrylonitrile electrolyte, the ionic conductivity was increased. The highest ionic conductivity was 2.3×10^{-4} S/cm in 10 wt% PAN-Al₂O₃ electrolyte at room temperature. The lithium yield of polymer electrolyte, interface resistance and bulk resistance decreased as adding inorganic filler and highest value was shown 0.29 which content 10 wt% PAN/EC/PC/LiClO₄/Al₂O₃. Inorganic filler promote polymer segmental motion for ion transport and decrease the interface resistance. Also it was shown that the yield of lithium ion is independent of the content of host polymer and amount of Al₂O₃. The interface resistance of PAN gel electrolyte showed minimum value at DC 5 mV.

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