

Electrochemical characteristics of bilayer film of polyaniline composite positive with polymer electrolyte binder/polymer electrolyte for Li-ion batteries

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Abstract

The bilayer film of polyaniline (PAN) composite positive/polymer electrolyte was prepared employing PAN powder as an active material and plasticized PEO-LiClO₄ with the ethylene carbonate (EC) and propylene carbonate (PC) plasticizer as an electrolyte. The micro-morphology and interfacial microstructure of the composite bilayer film were observed by scanning electron microscope (SEM). The effect of the content of polymer electrolyte on the homogeneity of the PAN composite positive film and the interfacial electrochemical kinetic parameters, the utilization ratio of the active material and discharge capacity were investigated. It was found that the contacting surface area between the PAN powder and the polymer electrolyte was greatly augmented by using polymer electrolyte as a binder. The PAN composite film with gel PEO-based polymer electrolyte (GPE) as the binder exhibited better interfacial compatibility, electrochemical reversibility than the PAN positive film with poly(tetrafluoroethylene) (PTFE) as the binder, and so the utilization ratio of the active material and the high rate discharge ability were observably improved. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polyaniline; PEO-based polymer electrolyte; Li-ion battery

1. Introduction

Polymer Li-ion battery is considered as the most advanced rechargeable battery technique because of its many advantages such as high energy density, high powder density, pollution-free and safety. Compared with liquid electrolyte-based Li-ion batteries, polymer lithium and/or Li-ion battery possesses the better shape flexibility and manufacturing integrity. Film-like polymer Li-ion batteries are especially propitious to be used in the smaller and lighter cellular phones and laptop computers, as well as in electric and/or hybrid vehicles.

Among the different polymer electrolytes described in the literatures, poly(ethylene oxide) (PEO) complex with lithium salts is the earliest and one of the most intensively studied polymer electrolytes for solid-state lithium or Li-ion batteries [1–5], as it is capable of dissolving a salt and ionizing it to produce charge carriers. But the low conductivity of PEO-based polymer electrolyte at ambient temperature excludes its practical applications. Several

methods, such as block copolymerization, grafting, cross-linking and plasticization have been introduced to improve the conductivity at ambient temperature. Plasticization of gel polymer electrolyte is a simple and effective method to improve the conductivity at room temperature. Many kinds of the gel-polymer electrolytes, such as poly(acrylonitrile), poly(methyl methacrylate), poly(ethylene oxide) and poly(vinylidene fluoride) with ethylene carbonate (EC), propylene carbonate (PC) as plasticizer, have been extensively investigated for their applications in polymer lithium or/and Li-ion batteries and electrochemical supercapacitors [6–8].

On the other hand, PAN is one of the intensively investigated conducting polymers [9,10], and has exhibited excellent electrochemical reversibility as a positive active material in either an aqueous or a nonaqueous electrolyte compared with any other conducting polymers. Many investigations have been concerned with the possibility of applying PAN to solid-state rechargeable lithium or Li-ion battery as a positive material [11–14]. It was found that PAN/PEO-LiClO₄ polymer electrolyte in a solid-state lithium battery exhibited a good electrochemical reversibility and cycleability at 50–80°C [12]. But in solid-state lithium-PAN battery, because that the active material could

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not sufficiently contact with polymer electrolyte and the contacting surface area between the active material and polymer electrolyte was the much lower than that in the liquid organic electrolyte. The utilization ratio of the positive active material was very low, about only 20% [12]. In order to improve the utilization ratio of the electroactive material, compatibility and reversibility of the interface between the electrode and polymer electrolyte, the composite electrode films were prepared by mixing of the active material with polymer electrode. Barthet et al. [15] prepared PAN composite positive with PEO-based polymer electrolyte as a binder for fabrication of a solid-state secondary lithium battery. Cyclic voltammetry and charge/discharge experiment were performed at 70°C. It was found that the above PAN composite positive with polymer electrolyte improved interfacial electrochemical characteristics and utilization ratio of the active material.

In the present work, we have prepared the bilayer film by employing polyaniline powder as a positive active material and plasticized PEO-LiClO₄ as a binder and polymer electrolyte. One side of this bilayer film is the PAN-GPE composite film, which is electronically and ionically conductive, and the other is a polymer electrolyte film, which is ionically conductive. The micro-morphology of the PAN composite film with polymer electrolyte binder and interfacial microstructure were observed by SEM. The effects of the polymer electrolyte contents in the PAN composite films on their homogeneity and the electrochemical kinetic parameters, discharge capacity and utilization ratio of active material at room temperature were discussed.

2. Experimental detail

2.1. Preparation of bilayer film of PAN-GPE composite positive/PEO-based polymer electrolyte

Polyaniline powders were chemically synthesized using (NH₄)₂S₂O₈ as an oxidant. An aqueous solution of 200 ml containing 0.4 M aniline + 1 M HClO₄ solution was added into a round flask, then 0.5 M (NH₄)₂S₂O₈ + 1.0 M HClO₄ solution of 50 ml was slowly added dropwise into the aniline solution with constant motor stirring at a reaction temperature of 0–5°C for 4 h. PAN powder was filtered and washed with distilled water until the filtrate was colorless, and then was doped with 0.1 M HClO₄ solution. The collected PAN powder was dried under a dynamic vacuum at 80°C for 48 h, and was milled to pass through a screen with 200 mesh. The bilayer film of PAN composite positive/PEO-based polymer electrolyte was prepared as follows. Above all, PAN-GPE composite positive film was prepared. The weighed PAN powder, dry poly(ethylene oxide) powder (average molecular weight 5,000,000, Aldrich Chemical Co., Inc.), anhydrous lithium perchlorate, EC and PC were added to a certain quantity of acetonitrile and subsequently stirred on a magnetic stirrer for 24 h, then the mixed slurry was

cast onto a Teflon board. The PAN composite positive film with PEO-based polymer binder was finally formed by evaporating the solvent of acetonitrile in flowing nitrogen atmosphere at room temperature for 48 h. Afterwards, the polymer electrolyte film was prepared on the PAN composite film as follows. PEO powder, anhydrous lithium perchlorate and a small quantity of EC and PC were added into a suitable quantity of acetonitrile. The mixture of the complex gel of PEO-LiClO₄ and PC + EC was sufficiently stirred by a magnetic stirrer for about 24 h, and then casted onto the PAN composite film. It was slowly dried under flowing nitrogen atmosphere for 24 h. The bilayer film was transferred into the vacuum and dried for 48 h to evaporate residual solvent. Its overall thickness was about 170 μm, in which, the PAN composite positive film was 100 μm thick, while the polymer electrolyte film was about 70 μm. The chemical composition of the gel polymer electrolyte was EO:LiClO₄:PC:EC = 10:1:3.8:3.6 by molar ratio. The micro-morphology of the composite film and interfacial microstructure between PAN composite positive and polymer electrolyte were observed by SEM. In order to measure the conductivity of the gel polymer electrolyte, a sandwich cell of Ni/(polymer electrolyte film)/Ni was assembled. The conductivity of the gel polymer electrolyte was measured to be about ~2 mS/cm at ambient temperature by the electrochemical impedance spectra using Solartron 1250 and Solartron 1286 system.

2.2. Measurement of electrochemical kinetic parameters and charge/discharge cycle

The gel-polymer Li-PAN battery was constructed by employing the bilayer film in an argon box, a lithium foil was used as a counter or reference electrode. The electrochemical kinetic parameters were measured by means of a potential step method. Cyclic voltammetry was performed using Solartron 1286 electrochemical interface at a scan rate of 1 mV/s. The charge/discharge cycles were carried out at room temperature by a galvanostat method. The battery was charged to 4.0 V and discharged to cut-off voltage of 2.5 V. High rate discharge ability was expressed as the ratio of discharge capacities at different discharge current densities to that at discharge current density of 0.1 mA/cm².

3. Results and discussion

3.1. Homogeneity, micro-morphology of PAN composite positive film and interface microstructure

Since, the PEO-based polymer electrolyte was used as both binder and ionic conductor in the PAN composite positive film, its content in the PAN composite film would strongly influenced the final formation, homogeneity and electrochemical performances of the film. Cherg et al. [16] found that the content of the polymer electrolyte was

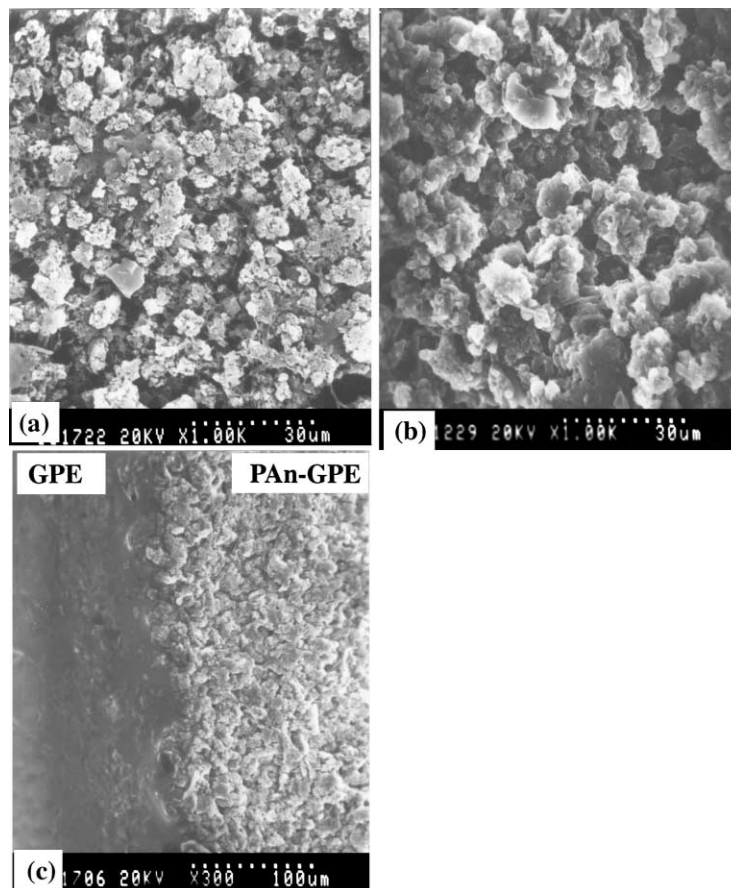


Fig. 1. SEM images of (a) the PAN film with PTFE binder, (b) the PAN composite film with PEO-based polymer electrolyte binder, and (c) the interfacial microstructure of PAN-GPE/polymer electrolyte.

required in 25–30 wt.% for preparing V_2O_5 composite positive with PEO-based polymer electrolyte binder. In the present work, if the content of the polymer electrolyte was <30 wt.%, the homogeneous PAN composite positive film could not be finally formed, and the cracks were produced on the PAN film. It was found that, in the range of the compositions of 65–40 wt.% PAN, 30–55 wt.% PEO-based polymer electrolyte and 5% acetylene black as conducting additive, the homogeneous PAN composite positive film could be finally formed.

The SEM micrographs of the PAN composite positive film with PEO-based polymer electrolyte binder and the PAN film with PTFE binder are shown in Fig. 1(a) and (b), in which one can see that PAN powder is uniformly distributed both in two type films. In case of PAN-PTFE film, if in a liquid organic electrolyte, the electrolyte could penetrate into the porous PAN-PTFE film. But in the solid-state or gel polymer electrolyte, the polymer electrolyte could not penetrate into the PAN-PTFE film. The active material PAN powder could not get an adequate touch with the polymer electrolyte and the contacting surface area between PAN and polymer electrolyte was lower. As a result, the compatibility and electrochemical reversibility of the interface of PAN-PTFE film/polymer electrolyte were decreased. Yang et al. [12] found that in

the Li/PEO-LiClO₄/PAN cell, the capacity of PAN was only 20 mAh/g at 80°C because of inadequate contacting between PAN and polymer electrolyte. In order to improve the electrochemical performances of the interface of PAN positive film/polymer electrolyte, an effective contact and a high contacting surface area between the active material PAN powder and polymer electrolyte is necessary. It is believed that the above mentioned method is an effective method to prepare the PAN composite film with polymer electrolyte binder. The interfacial microstructure between PAN composite positive and polymer electrolyte is shown in Fig. 1(c), in which one can see that the PAN powder can get in good touch with the polymer electrolyte, and by this way the polymer electrolyte binder inside PAN composite film and polymer electrolyte can contact with each other. The interfacial contacting area is greatly increased. As a result, there is a high probability that the compatibility, electrochemical reversibility and utilization of active material are greatly improved.

3.2. Cyclic voltammetry and electrochemical kinetic parameters of bilayer film

Cyclic voltammograms of the PAN-PTFE/PEO-based polymer electrolyte film and PAN-GPE/PEO-based polymer

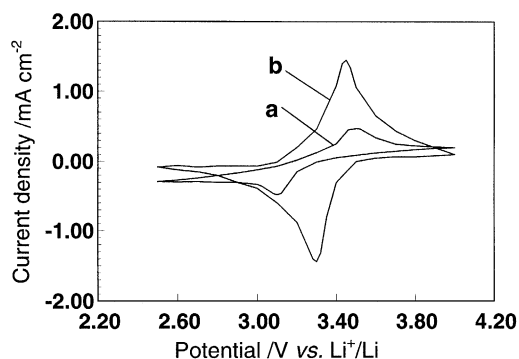


Fig. 2. Cyclic voltammograms of (a) the PAN-PTFE/polymer electrolyte, and (b) the PAN-GPE (45%)/polymer electrolyte at a scan rate of 1 mV/s.

electrolyte film are shown in Fig. 2. It can be seen from Fig. 2 that the anode and cathode peaks currents and areas of PAN-GPE composite positive film are much larger than those of PAN-PTFE film. It means that the charge and discharge capacity of PAN-GPE film is larger than that of PAN-PTFE film during cyclic voltammetry. In addition, the anode peak potential of PAN composite film with polymer electrolyte binder is nearer to its cathode peak potential compared with PAN-PTFE film. The fact means that PAN composite film with polymer electrolyte binder has better compatibility and electrochemical reversibility than PAN-PTFE film.

The electrochemical kinetic parameters of PAN-PTFE and PAN-GPE composite films measured by means of the potential step are summarized in Table 1. Above all, the charge transfer resistance (R_F) of PAN-GPE film is lower than that of PAN-PTFE film, and the exchange current densities (i_0) of PAN-GPE film is larger than that of PAN-PTFE film. The greater double layer capacity (C_{dl}) of PAN-GPE/polymer electrolyte means that the bilayer composite film has a larger contacting specific surface than the PAN-PTFE/polymer electrolyte. These facts indicate that PAN composite positive with polymer electrolyte binder greatly augment the contacting surface area between PAN and polymer electrolyte, and so improve its electrochemical performances. In addition, it can be also seen from Table 1 that the exchange current density increases with increasing the content of PEO-based polymer electrolyte in PAN composite film, until approaching a maximum value at 45–50 wt.% of the content

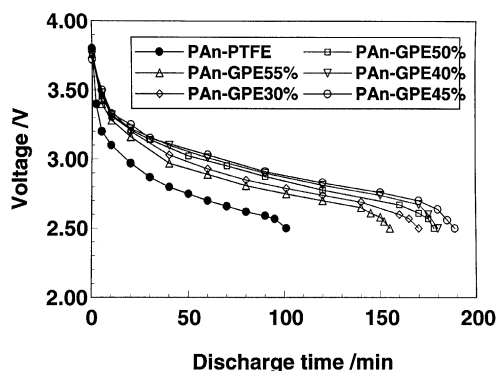


Fig. 3. Typical discharge curves of the Li/GPE/PAN-PTFE and the Li/GPE/PAN-GPE batteries at room temperature (charge to 4.0 V and discharge to 2.5 V at a constant current density of 0.2 mA/cm²).

of polymer electrolyte. Then as the content of polymer electrolyte exceeds 50%, the exchange current density decreases. It is likely that the part of active material PAN powder is separated by overmuch polymer electrolyte, which cannot participate in the electrode reaction.

3.3. Charge/discharge performance of polymer Li-PAN batteries

Typical discharge curves of Li/GPE/PAN-PTFE and Li/GPE/PAN-GPE batteries are shown in Fig. 3. The effects of the content of PEO-based polymer electrolyte in PAN-GPE composite film on the discharge capacity and utilization ratio of the active material are summarized in Table 2. Above all, it can be seen from Fig. 3 and Table 2 that the PAN composite films with polymer electrolyte binder have larger discharge capacities and utilization ratios than the PAN-PTFE. Moreover, the discharge capacity and utilization ratio of the active material PAN are increased with increasing the content of polymer electrolyte binder. At 45–50% of the content of polymer electrolyte, the maximum discharge capacity and utilization ratio are up to about 45–49 mAh/g PAN and 39–42%, respectively, this capacity value based on PAN is very close to that of ~50 mAh/g in EC:DEC 1 M LiPF₆ electrolyte reported by Ryu et al. [17]. Although, the specific capacity based on the cathode mass is only ~25 mAh/g as shown in Table 2, it can be used as the power sources for memory back-up and small electronic

Table 1
Effect of polymer electrolyte in PAN composite films on the electrochemical kinetic parameters of PAN composite/polymer electrolyte bilayer film

Sample no.	Content of GPE in PAN composite film (%)	R_F (Ω cm ²)	i_0 (mA/cm ²)	C_{dl} (μ F/cm ²)
1	Content of PTFE 7%	112	0.11	94
2	30	65.0	0.20	1077
3	40	42.5	0.31	1400
4	45	27.3	0.47	1907
5	50	27.0	0.46	2155
6	55	51.1	0.25	2123

Table 2
Effect of polymer electrolyte in PAN-GPE composite films on the capacity and utilization ratio of PAN

Sample no.	Content of GPE in composite film (%)	Capacity (mAh/g PAN)	Capacity (mAh/g electrode)	Utilization ratio (%)
1	Content of PTFE 7%	21.2	20.2	19.1
2	31	27.9	19.5	24.1
3	40	35.9	21.5	31.2
4	45	45.3	24.9	39.3
5	50	49.1	24.6	42.4
6	55	44.7	21.1	38.2

machines, because of the long cycle life, less self-discharge rate, endurance to overdischarge, low cost for manufacture, flexible shape and ease to make thin films [18]. As the content of polymer electrolyte exceeds 50%, the discharge capacity and utilization ratio slightly decrease. The discharge capacities of Li-PAN cell as a function of cycles number at room temperature are shown in Fig. 4. It is found from Fig. 4 that both PAN-GPE composite and PAN-PTFE positive have good cycle stability before 200th cycle.

High rate discharge ability of the PAN-PTFE and the PAN-GPE composite positive is shown in Fig. 5. It is found from Fig. 5 that the PAN composite with polymer electrolyte binder exhibits better high rate discharge ability than

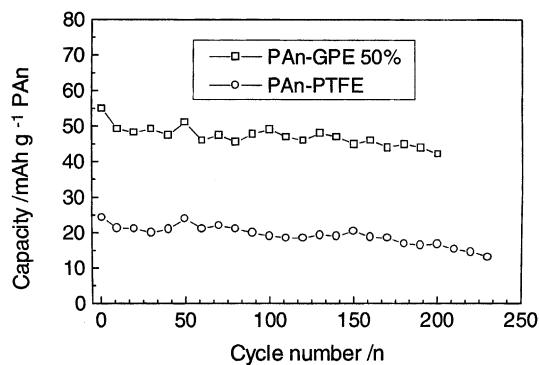


Fig. 4. Discharge capacity of the Li-PAN cell as a function of cycles number at room temperature at a constant current density of 0.2 mA/cm².

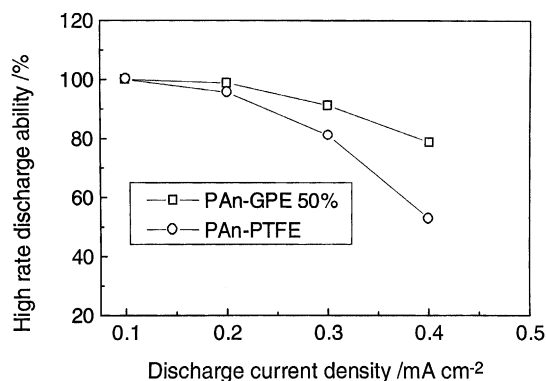


Fig. 5. High rate discharge ability of the PAN-PTFE and the PAN composite with polymer electrolyte binder.

PAN-PTFE. It is likely that by using polymer electrolyte as the binder, the contacting surface area between PAN and polymer electrolyte was markedly augmented. Moreover, the polymer electrolyte in the PAN composite film could provide the path for ion diffusion during electrochemical reaction. Therefore, high rate discharge ability of the PAN composite positive are greatly improved.

4. Conclusion

The bilayer film of PAN-GPE composite positive/PEO-based polymer electrolyte was prepared, which is an interesting candidate for polymer lithium and Li-ion batteries. As the content of the polymer electrolyte in the PAN composite positive film was from 30 to 55% by mass ratio, the PAN composite film could homogeneously formed. It was found that the contacting surface area between PAN and polymer electrolyte was greatly improved by employing polymer electrolyte as the binder. The PAN composite positive film exhibited the more compatibility and electrochemical reversibility than that of PAN film with PTFE binder. As a result, the discharge capacity and utilization ratio of the PAN active material were remarkably improved.

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References

- [1] D.E. Fenton, J.M. Parker, P.V. Wright, *Polymer* 14 (1973) 589.
- [2] M. Armand, M. Duclot, French Patent 78,329,76 (1978).
- [3] S. Izuchi, S. Ochiai, K. Takeuchi, *J. Power Sources* 68 (1997) 37.
- [4] P. Lightfoot, M.A. Mehta, P.G. Bruce, *Science* 263 (1993) 883.
- [5] G.S. MacGlashan, Y.G. Andreev, P.G. Bruce, *Nature* 398 (1999) 792.
- [6] W.H. Meyer, *Adv. Mater.* 10 (1998) 439.
- [7] J.Y. Song, Y.Y. Wang, C.C. Wan, *J. Power Sources* 77 (1999) 183.
- [8] T. Osaka, X. Liu, M. Nojima, T. Momma, *J. Electrochem. Soc.* 146 (1999) 1724.
- [9] E.M. Genies, A. Boyle, M. Lapkowski, C. Ysinavis, *Synth. Met.* 36 (1990) 139.

- [10] N. Gospodinova, L. Terlemezyan, *Progr. Polym. Sci.* 23 (1998) 1443.
- [11] A.G. MacDiarmid, L.S. Yang, W.S. Huang, B.D. Humphery, *Synth. Met.* 18 (1987) 393.
- [12] L.S. Yang, Z.Q. Shan, Y.D. Liu, *Solid-State Ionics* 40/41 (1990) 967.
- [13] L.S. Yang, Z.Q. Shan, Y.D. Liu, *J. Power Sources* 34 (1991) 141.
- [14] L.S. Yang, Z.Q. Shan, P.M. Hou, W.X. Chen, L. Liu, *J. Power Sources* 43/44 (1993) 499.
- [15] C. Barthelet, M. Guglielmi, P. Baudry, *J. Electroanal. Chem.* 431 (1997) 145.
- [16] J.Y. Cherng, M.Z.A. Munshi, B.B. Owens, W.H. Smyrl, *Solid-State Ionics* 28–30 (1988) 857.
- [17] K.S. Ryu, K.M. Kim, S.G. Kang, J. Joo, S.H. Chang, *J. Power Sources* 88 (2000) 197.
- [18] K.S. Ryu, K.M. Kim, S.G. Kang, G.J. Lee, J. Joo, S.H. Chang, *Synth. Met.* 110 (2000) 213.