

Conductive Bilayer Polymer Films Formed by Polyaniline and Polymeric Ionic Conductor

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ABSTRACT: Conductive bilayer polymer films based on polymer electrolyte and polyaniline have been prepared by the electrochemical polymerization of aniline on an electrode covered with an ionic conductive polymer film. Electrochemical polymerization was carried out by the potentiodynamic method. The electrochemical properties of the bilayer films were investigated by cyclic voltammetry. The cyclic voltammograms indicated that the bilayer films have good redox stability, as well as reversibility, and show electrochemical activity in the solid state at room temperature. An all-solid-state rechargeable battery composed of lithium and this bilayer polymer film was tested. The preliminary experimental results showed that the battery can discharge in moderate electric current. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 537–541, 1997

Key words: conductive polymer; polymer electrolyte; electropolymerization; all-solid-state rechargeable battery

INTRODUCTION

Many approaches have been used to circumvent the processing difficulties encountered with electronic conducting polymers, such as polypyrrole, polythiophene, and polyaniline. These include the grafting the conducting polymer chain to a nonconductive (but easily processable) polymer, deriving the polymer by incorporating long side groups into the aromatic ring, and making blends or composites of conductive and nonconductive polymers,^{1–4} etc. However, these techniques often yield materials with conductivities much lower than the parent polymers. Watanabe⁵ et al. reported the electrochemical polymerization of pyrrole using ion-conducting polymers as a solid electrolyte and prepared polypyrrole/polymer electrolyte bilayer composite *in situ*.

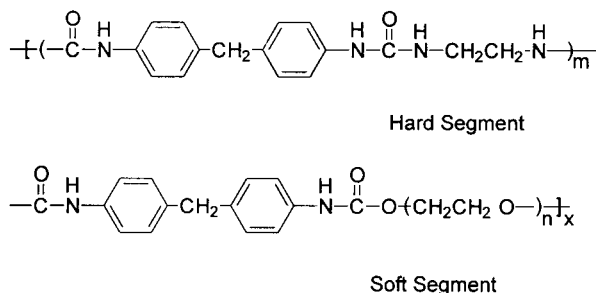
The research of polymer solid electrolytes has been widely expanded since Wright reported that

the complexes of poly(ethylene oxide) (PEO) and alkali-metal salts showed good ionic conductivity.⁶ However, the PEO-based solid electrolytes have several disadvantages, such as low conductivity in ambient temperature, poor mechanical properties, etc. We have developed a novel host polymer, poly(ethylene glycol)-type segmented polyether polyurethaneurea (PEUU). The ionic conductivities of the complexes of PEUU and LiClO₄ are one to two orders of magnitude higher than those of the PEO-based solid electrolytes at ambient temperature. The polymer film electrolytes have excellent resistivity against water and better adherence to electrodes, as well as good mechanical strength.⁷

In this article, we present a route to prepare conductive polymer bilayer films with dual functions and the final desired shape. We also report the performance of an all-solid-state rechargeable battery composed of lithium and polyaniline—PEUU–LiClO₄ bilayer films. In this battery system, lithium is used as anode; the polyaniline layer and PEUU–LiClO₄ layer are used as a cathode and an electrolyte, respectively.

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Scheme 1 Chemical structure of PEUU matrix.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG; $M_n = 1000$) was dried at 70°C in a vacuum oven for 72 h; 4,4'-methylenedi(phenyl methane isocyanate) (MDI), and ethylenediamine (EDA) was purified by vacuum distillation; aniline was purified by vacuum distillation under the nitrogen atmosphere.

Preparation of the PEUU-LiClO₄ Film Electrolyte

PEUU matrix was synthesized from MDI, EDA, and PEG. The molar ratio of MDI : EDA : PEG was 2 : 1 : 1, which resulted in the hard segment content of 35 wt %. Full details are presented elsewhere.⁸ The chemical structure of PEUU matrix is illustrated in Scheme 1.

Uniform thickness (100 μm) and bubble-free films of PEUU-LiClO₄ were prepared by solution casting in DMA on a Teflon plate. After the solvent had been evaporated at 60–70°C, the films were transferred to a vacuum oven at 70°C for at least four days to remove the residual solvent. The concentration of LiClO₄ in the PEUU-LiClO₄ complexes was expressed by the molar ratio of LiClO₄ to the ethylene oxide (EO) repeating unit of PEUU. The ratio of [LiClO₄]/[EO unit] in this article is 0.05.

Preparation of the Bilayer Films

The bilayer film was prepared by electrochemical polymerization of aniline on an electrode wrapped with the PEUU-LiClO₄ film in a single-compartment three-electrode cell at ambient temperature under potentiodynamic conditions. The working electrode was a platinum disk (15 mm diameter) covered with the PEUU-LiClO₄ film. A platinum plate was used as the counter electrode, and a

saturated calomel electrode (SCE) was as reference electrode. The electrolytic solution was 0.4 mol/dm³ aniline and 1.2–2.3 mol/dm³ HClO₄ aqueous solution. The potential sweep ranges were between -0.2 and 1.4 V versus SCE at a scan rate of 20 mV/s. After the electropolymerization, the working electrode was rinsed with water and dried at room temperature. The bilayer films were then removed from the working electrode.

Characterization of the Bilayer Films

The electronic conductivity of polyaniline (PAn) layer was measured using the four-probe method.

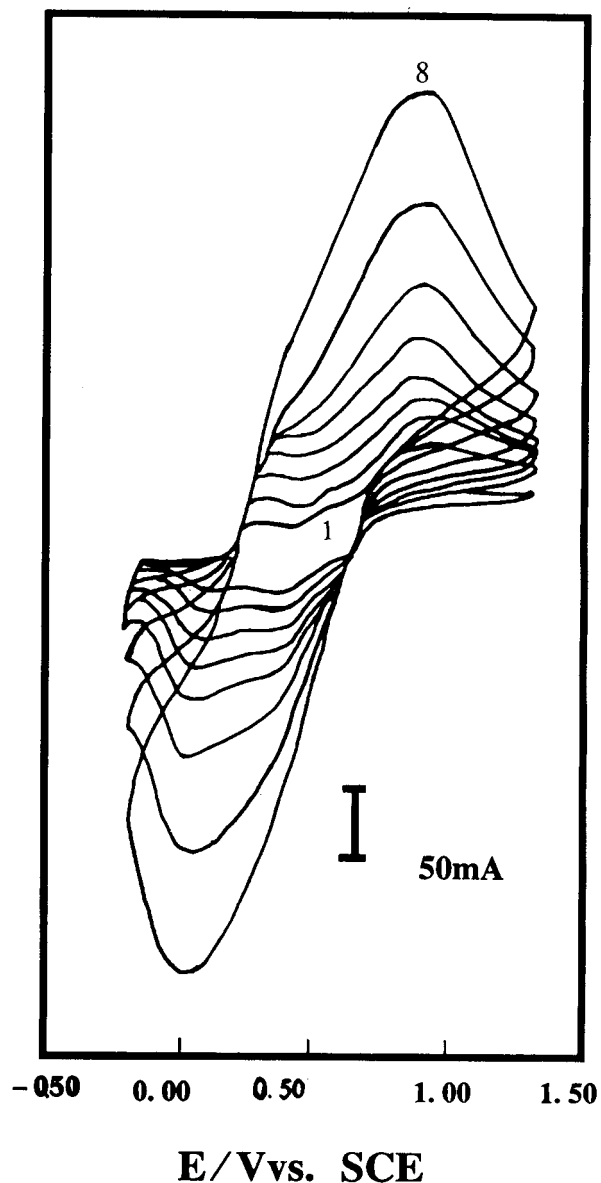


Figure 1 Cyclic voltammograms recorded during potentiodynamic aniline polymerization on a PEUU-LiClO₄ film-covered Pt working electrode.

The ionic conductivity of the polymeric electrolyte layer was measured with a Hewlett-Packard Model 4192A LF impedance analyzer and analyzed by complex impedance techniques between 5 Hz and 13 MHz.

Scanning electron micrographs (SEM) were obtained on a Hitachi X-650 scanning electron microscope at an accelerating voltage of 20 kV.

The bilayer films were investigated by cyclic voltammetry. Instrumentation for the cyclic voltammetric experiments consisted of a DH-2 Model multifunctional constant potentiometer and a Yokogawa Hokushin Electric Type 3086 X-Y recorder. The electrolytic solution for the cyclic voltammetry was 1 mol dm³ ZnCl₂ aqueous solution containing 0.5 mol/dm³ NH₄Cl, 0.1 mol/dm³ NaBF₄, and certain amount of HCl. The working, counter, and reference electrodes are PEUU-LiClO₄-PAn bilayer films, Pt plate, and SCE, respectively. Measurement was made at a scan rate of 6 mV/s and at room temperature.

Battery Construction and Cycling

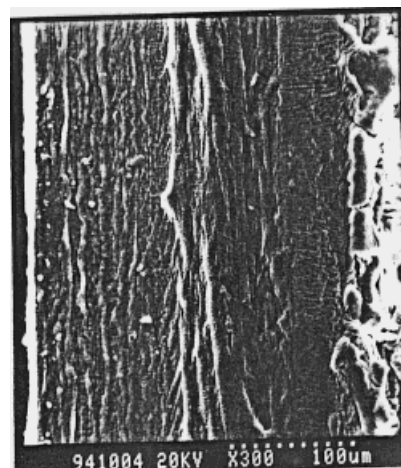
The fabrications of the batteries were carried out in a < 5% RH glove box. All-solid-state, thin-film, Li/PAn batteries were constructed with the PEUU-LiClO₄-PAn bilayer films (PAn layer and PEUU-LiClO₄ layer were used as cathode and solid electrolyte, respectively) and a lithium (99.99%) foil. The battery cell was positioned between matching nickel plate current collectors. All of them were pressed and sealed into the battery house made of stainless steel. The discharge was carried out at a constant current density of 280 μA/cm². Discharge of the cell was terminated when the battery voltage reached 2.0V. Then the battery was charged at a constant voltage of 5.0V. The end point voltage of charge was not more than 3.8V.

RESULTS AND DISCUSSION

Electrochemical Polymerization at Electrodes Covered with PEUU-LiClO₄ Film

Typical cyclic voltammograms (CVs) of the electrochemical polymerization of aniline on a Pt electrode covered with PEUU-LiClO₄ film are shown in Figure 1.

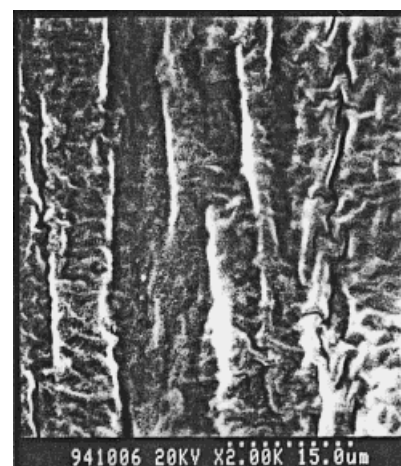
The cyclic voltammogram curves in the six initial cycles show two pairs of redox current peaks. As the number of cycles increases, the peak cur-



(a) bilayer films



(b) PEUU-LiClO₄ layer



(c) PAn layer

Figure 2 Scanning electron micrographs of a cross section of PEUU-LiClO₄-PAn bilayer films: (a) bilayer films; (b) PEUU-LiClO₄ layer; (c) PAn layer.

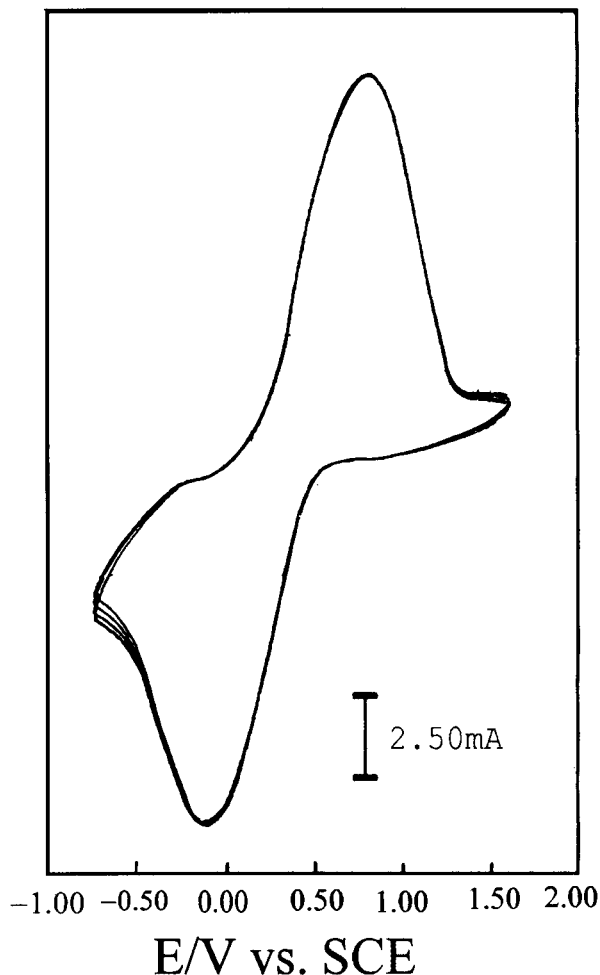


Figure 3 Cyclic voltammograms of PEUU-LiClO₄-PAN bilayer films.

rent increases, indicating the growth of polyaniline; both the oxidation peaks and the reduction peaks fuse into one; the Pt electrode side of the PEUU-LiClO₄ film becomes dark green, but the solution side is still light yellow. On repeating the same experiment with a bare Pt working electrode, very similar CV curves are observed. These experimental results showed that the aniline molecules could pass through the pores of the PEUU-LiClO₄ film to the surface of the Pt electrode, then polymerize at the Pt surface and grow to the surface of PEUU-LiClO₄ film. After 15–25 min of electrochemical polymerization, the bilayer films can be peeled easily from the Pt electrode and handled as elastic film.

The scanning electron micrographs of the cross section of a PEUU-LiClO₄-PAN bilayer-film are shown in Figure 2.

In Figure 2(a), the right side indicates the

polyaniline layer, and the left, the PEUU-LiClO₄ layer. Figure 2(a) shows that the middle portion is a transition zone, which contains both the PAN and the PEUU-LiClO₄ complex. The PAN layer prepared by the electrodeposition has a lamellar structure, as clearly shown in the SEM micrograph [Fig. 2(c)] for the cross section through the thickness of the PAN layer.

The electronic conductivity of PAN layer in the bilayer films is influenced by many factors. Under our experimental conditions, electronic conductivity, which was measured by four-probe method, reached 30 S/cm. The electronic conductivity of PAN layer remained unaltered when the bilayer films stood in air for a few months. It had one order of magnitude lowering after three years in air. The ionic conductivity of the polymeric electrolyte layer was in the order of 10⁻⁵ S/cm at ambient temperatures.

Figure 3 shows cyclic voltammogram of the PEUU-LiClO₄-PAN bilayer films at a scan rate of 6 mV/s. The cyclic voltammograms indicated that the bilayer films have good redox stability, as well as reversibility, and show electrochemical activity in solid state at room temperature.

The typical charging-discharging curve of the all-solid-state, rechargeable battery composed of Li/PEUU-LiClO₄-PAN bilayer film is shown in Figure 4. The discharge of the cell was conducted at 50 ± 1°C with a constant current of 280 μA/cm². Table I shows the temperature effect upon

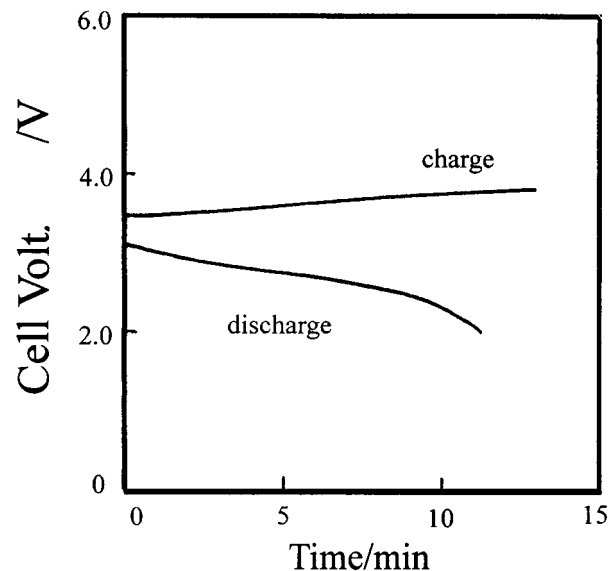


Figure 4 Typical curve of charge and discharge for an all-solid-state lithium battery utilizing the bilayer films: 11th cycle; CD = 280 μA/cm²; 50°C.

Table I Temperature Effect on Open Circuit Voltage and Short Circuit Current for An All-Solid-State Battery

Temperature (°C)	Open Circuit Voltage (V)	Short Circuit Current ($\mu\text{A}/\text{cm}^2$)
20	3.07	224
30	3.30	589
40	3.32	1115
50	3.35	2317
60	3.35	5813
70	3.32	7480

open circuit voltage and short circuit current of the cell. As it is now well known, the complexes of PEO and LiSO_3CF_3 or LiClO_4 , are useful battery electrolytes above 80°C ; but at room temperature, the conductivity of PEO- LiSO_3CF_3 or PEO- LiClO_4 is too low for those materials to be used in practical cells. Between room temperature and 80°C , the conductivity of PEUU- LiClO_4 complexes is one to two orders of magnitude larger than that of the poly(ethylene oxide) systems. Thus, in contrast to the PEO-based electrolytes, the new PEUU- LiClO_4 electrolyte is a good candidate for a room temperature solid-state battery. It has been proved to be of utmost importance for the overall performance of any solid-state batteries that interfaces between electrolyte film and electrodes have the good interfacial integrity, in which electrolyte film is thin and uniform, and in which the cathode has high porosity as well as good strength. The results presented here indicate that this type of dual functional film consisting of electronic conductor layer and ionic conductor layer has the good interfacial integ-

rity critical to the overall performance of any solid-state battery.

CONCLUSION

We have developed a new approach for preparing dual functional film consisting of electronic conductor layer and ionic conductor layer. Furthermore, the bilayer films have good interfacial integrity, which is critical to the overall performance of any all-solid-state cell. Besides making a thin film rechargeable battery, this bilayer polymer film may be a good candidate for electrochromic display devices, molecular transistors, and molecular electronics elements. It also supplies a new object of studying solid-state electrochemistry.

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