Charge/discharge characteristics of polyaniline-based polymer composite positives for rechargeable lithium batteries

Masayuki Morita [a,*], Seijiro Miyazaki [a], Masashi Ishikawa [a], Yoshiharu Matsuda [a], Hidehiko Tajima [b], Kazuyuki Adachi [c], Fumimasa Anan [c]

[a] Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755, Japan
[b] Nagasaki Research and Development Center, Mitsubishi Heavy Industries, Ltd., 5-717-1 Fukahori-machi, Nagasaki 851-03, Japan
[c] Research Laboratory, Kyushu Electric Power Company, Inc., 2-1-47 Shiobaru, Minami-ku, Fukuoka 815, Japan

Abstract

The structure of a polyaniline–poly(styrene-4-sulfonate) (PAn–PSS) composite film was optimized as the positive electrode for rechargeable lithium batteries to improve the charge/discharge characteristics in organic electrolyte solutions. The composite films prepared in aqueous poly(styrene-4-sulfonic acid) (PSSH) solutions containing small amounts of $HClO_4$ showed higher charge/discharge capacities than those prepared in PSSH without $HClO_4$. However, the utilization of Li^+-ion transport in the redox process decreased with an increase in the $HClO_4$ concentration. A stacked PAn–ClO_4/PAn–PSS film, which consists of an inner PAn layer doped with smaller size anion (ClO_4^-) and an outer PAn–PSS composite layer, was prepared by the electrolysis of aniline in aqueous $HClO_4$ followed by the polymerization in a PSSH solution. The resulting films gave improved charge/discharge characteristics in organic electrolyte solutions and lead to higher energy density of the full cell with lithium negative electrode.

Keywords: Rechargeable lithium batteries; Polyaniline

1. Introduction

There have been many studies on the application of various electroconducting polymers to the electrode materials of rechargeable lithium (Li) batteries. Among them, much attention has been directed to the polymers containing ionomers like poly(styrene-4-sulfonate) (PSS) as immobilized dopants because the resulting battery systems should have higher energy densities than those using conventional polymers containing mobile anion dopants [1]. In spite of many studies on the electroconductive polymer–ionomer composites in aqueous electrolyte systems, limited work has been published for the composites in non-aqueous organic electrolytes, except for the papers about polypyrrole (PPy)–PSS [2–4], PPy–Nafion® [5] and polyaniline (PAn)–Nafion® [6,7] composites.

The PAn-based polymer composites have the highest potential energy density [8,9]. We studied the basic polarization behavior of PAn–PSS composite films in organic electrolyte solutions [9]. The discharge capacity

of the PAn–PSS in organic solutions was much lower than that of the conventional p-type (anion exchanging) PAn. In this work, therefore, we have first attempted to optimize the composite structure and improved the charge/discharge cycling performances. That is, relationships between the synthetic conditions of PAn–PSS and the battery performances were investigated. Next, layered (or stacked) composite films consisting of PAn–X (X: low molecular weight anions) and PAn–PSS were synthesized by consecutive electrochemical polymerization. Their basic redox behavior and charge/discharge characteristics were investigated in organic electrolyte solutions.

2. Experimental

The PAn–PSS composite films were prepared on a platinum sheet substrate by anodic oxidation of aniline in aqueous PSSH solution. The electrolysis was carried out under constant-current conditions (usually, the current density was 0.25 mA cm^{-2} and the quantity of electricity was 0.6 C cm^{-2}). An appropriate amount

* Corresponding author.

of $HClO_4$ was added to the electrolyte to control the amount of the sulfonate group in the composite. For comparison, conventional PAn doped with a mobile anion (PAn–ClO_4) was prepared in a similar manner from an aqueous $HClO_4$ solution without PSSH.

The layered composite films were formed by stepwise electrooxidation in different electrolyte systems. First the PAn–X (X = ClO_4, Cl, etc.) films were polymerized on a platinum sheet substrate by constant-current oxidation of aniline in aqueous HX solutions. Then the PAn–PSS layer was deposited on the PAn–X films by the polymerization of aniline from PSSH-containing solutions. The total amounts of the deposited films, which will be represented as PAn–X/PAn–PSS, were equivalent to the quantity of electricity of 0.6 C cm^{-2}. In some cases, the resulting composites were treated with a mixed dimethylsulfoxide–dimethylformamide (DMSO–DMF) solvent before the electrochemical measurements.

The electrochemical properties were examined by cyclic voltammetry (CV) using a three-electrode cell equipped with an Li counter and Li/Li$^+$ reference electrodes [5,9]. The electrolyte solution was a mixture of propylene carbonate (PC) (or ethylene carbonate (EC)) and 1,2-dimethoxyethane (DME) (50/50 by volume) dissolving 1 M LiClO$_4$. The charge/discharge cycling was carried out under constant-current conditions. These electrochemical measurements were conducted in a dry argon atmosphere at room temperature (18–25 °C).

3. Results and discussion

3.1. Activation of PAn–PSS composite films

The polymer composites containing sulfonate ($-SO_3^-$) groups generally show low redox activity in organic electrolyte solutions [3,9]. As the sulfonate group in the composite includes hydration water, the excess amounts of incorporated sulfonate inhibit the redox process accompanied by the transport of the solvated cation (Li$^+$) in the polymer. We have attempted here to control the amount of the sulfonate group in the composite. The PAn–PSS composite films were prepared from aqueous PSSH solutions (the acid concentration was equivalent to 0.3 M) in which different amounts of $HClO_4$ were contained. Fig. 1 shows the variation of the discharge capacity measured in LiClO$_4$ (1 M)/PC+DME with the concentration of $HClO_4$ in the solution for film preparation. The discharge capacity increased with increasing the $HClO_4$ concentration in the solution. Fig. 2 summarizes the effects of the electrolyte composition on the discharge capacity of PAn–PSS. When the electrolyte did not contain $HClO_4$, a maximum capacity (~20 mC cm^{-2}) was observed at
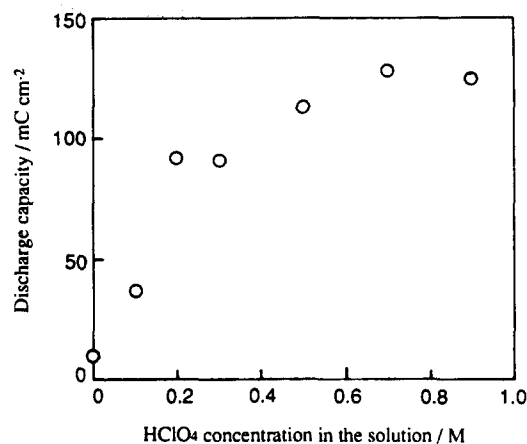

Fig. 1. Discharge capacity of PAn–PSS measured in LiClO$_4$/PC+DME as a function of $HClO_4$ concentration in the electrolyte for the film preparation. The solution consists of aniline 0.25 M, PSSH ($-SO_3^-$ concentration: 0.3 M) and $HClO_4$.
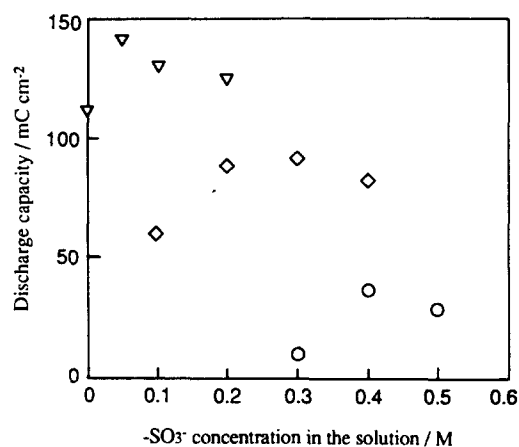

Fig. 2. Discharge capacity of PAn–PSS measured in LiClO$_4$/PC+DME as a function of $-SO_3^-$ concentration in the electrolyte for film preparation. The solution consists of aniline (0.25 M), PSSH, and $HClO_4$ ((○) 0 M; (◇) 0.2 M, and (∇) 1.0 M).

0.4 M of $-SO_3^-$ concentration. On the other hand, the PAn–PSS films prepared in the solutions containing 0.2 or 1.0 M $HClO_4$ showed much higher capacities. The highest capacity (~140 mC cm^{-2}) observed for the film formed in 1.0 M $HClO_4$ and 0.05 M $-SO_3^-$ is equivalent to 170 Ah kg^{-1}, which is almost the same as that reported as a theoretical maximum capacity for PAn electrodes [8].

The X-ray photoelectron spectroscopy (XPS) analyses of the composite films proved that the $-SO_3^-$ content incorporated in the film decreased with the $HClO_4$ concentration in the electrolyte for film preparation. Thus, the addition of $HClO_4$ in the electrolyte suppressed the excess doping of sulfonate in the composite. The discharge capacity was improved by controlling the $-SO_3^-$ content in the polymer, but the utilization of Li$^+$-ion transport in the charge/discharge process was rather low for the polymers formed in the solutions with high $HClO_4$ concentration.

Osaka et al. [3] reported that the potential cycling in DMF promoted the solvent exchange in the PPy–PSS composite and then improved the electrochemical activities of PPy–PSS in PC-based electrolytes. Similar pretreatments using a high donicity solvent were effective to the PAn–PSS composites prepared in aqueous electrolytes. Fig. 3 shows the discharge capacities of the PAn–PSS composites treated by dipping in DMSO–DMF(5:1 by volume) before measurements. Higher capacities were observed for the electrodes treated by DMSO–DMF, even though the electrodes were prepared in the PSSH solutions without HClO₄.

3.2. Layered PAn–X/PAn–PSS composite

The idealized redox process of the present double-layer composite is schematically shown in Fig. 4. The composite film consists of stacked two layers: the inner one is PAn with low molecular weight anion (X) as the dopant, and the outer contains higher molecular-weight ionomer (PSS) as the immobilized dopant. In this type of composites, cation (Li^+) transfer should be the charge compensation process during the electrochemical oxidation/reduction cycle because the outer PAn–PSS layer act as a cation-permeable membrane. The resulting battery systems using these composite polymer cathodes have potentially higher energy densities than the batteries using conventional PAn–X or PAn–ionomer single films because the system employs a light-weight cathode and a minimum amount of electrolyte.

Fig. 5 shows typical CV curves of the layered PAn–ClO₄/PAn–PSS composite, in which the equivalence ratio of two layers was 1/1. Fig. 5 includes the curve of PAn–ClO₄ for comparison. The PAn–ClO₄/PAn–PSS composite showed essentially the same CV profile as that of single PAn–ClO₄. That is, each curve

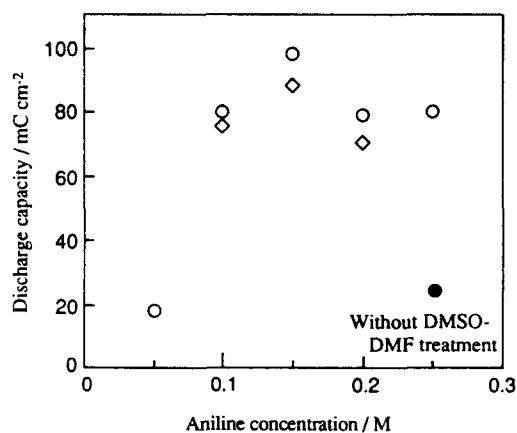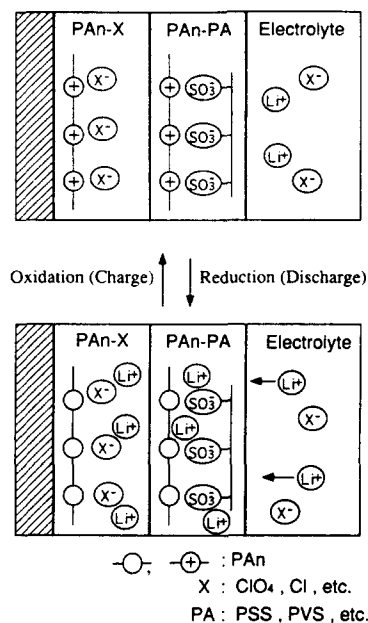Fig. 4. A schematic model for charge compensation in layered PAn–X/PAn–PSS composite films.
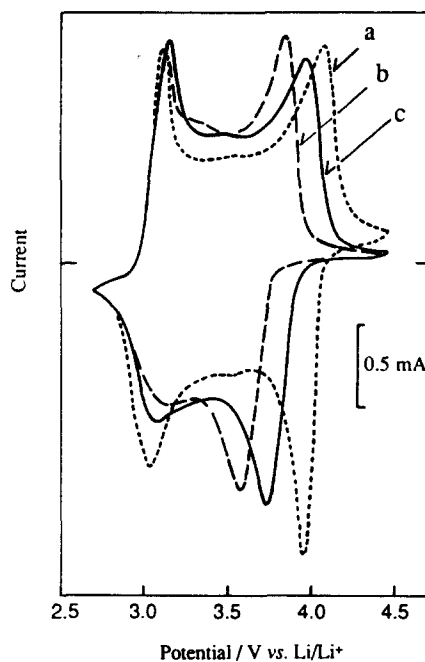
Fig. 5. Cyclic voltammograms for PAn–ClO₄ and PAn–ClO₄/PAn–PSS films in LiClO₄(1 M)/PC + DME. Potential scan rate: 10 mV s⁻¹. (a) PAn–ClO₄; (b) PAn–ClO₄/PAn–PSS without treatment, and (c) PAn–ClO₄/PAn–PSS with DMSO + DMF treatment.

Fig. 3. Discharge capacity of PAn–PSS measured in LiClO₄/PC + DME after DMSO + DMF treatment as a function of aniline concentration in the electrolyte for film preparation. The solution consists of aniline and PSSH (–SO₃⁻ concentration: (◇) 0.4 M, and (○) 0.5 M).

consists of two main redox couples, which means the electrochemical redox reaction of the layered composite film contains two-electron transfer like that of the conventional PAn films. However, there were some differences in the peak potentials, especially for the redox couple at more positive potential. The layered PAn–ClO₄/PAn–PSS composite showed the anodic and cathodic peaks at about 3.7 and 3.6 V versus Li/Li⁺,
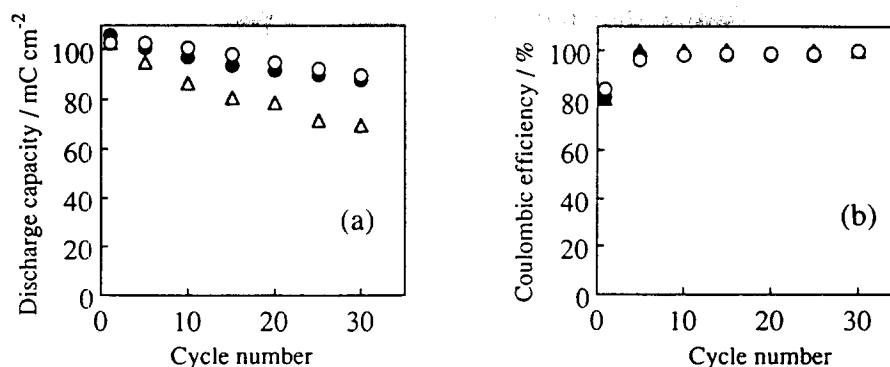
Fig. 6. (a) Discharge capacity and (b) coulombic efficiency for the charge/discharge cycling of PAn–ClO₄/PAn–PSS (1/1): (O) in LiClO₄-(1 M)/PC + DME after PC + DME rinsing; (●) in LiClO₄(1 M)/EC + DME after EC + DME rinsing, and (△) in LiClO₄(1 M)/PC + DME without PC + DME rinsing.

respectively, while the single PAn–ClO₄ film at about 4.0 V. The peak potential of the layered composite was shifted to more positive by treating the film with mixed DMSO–DMF. This phenomenon was considered to relate with some changes in the solvation of the ion-exchange sites in the PAn–PSS layer [3,9].

The electron-probe microanalysis (EPMA) spectra of the PAn–ClO₄/PAn–PSS film revealed that the dopant ClO₄⁻ was immobilized in the film during the electrochemical oxidation and reduction in the organic electrolytes, while the charge compensation process in single PAn–ClO₄ was the anion transfer. The Li contents in the films, measured by elemental analysis, showed that the Li⁺-ion transfer in the film contributes to the charge compensation during the redox process of the layered composite film. The Li⁺-ion transport number in the process depended on the film composition, e.g., the mass ratio of PAn–X and PAn–PSS in the composite.

Fig. 6 shows the results for the charge/discharge (electrochemical oxidation and reduction) cycling of the layered PAn–ClO₄/PAn–PSS (1/1) composite under a constant current density (0.1 mA cm⁻²). The discharge capacities of ~100 mC cm⁻² or higher were obtained in the initial cycles. These are equivalent to the specific capacities of ~120 Ah kg⁻¹ or higher (the calculation is based on the PAn mass), and were about four times of the capacities of PAn–PSS single films [9]. The discharge capacity tended to decrease with the repeated cycles, especially in case of films without rinsing by the test solvents after the DMSO–DMF pretreatment. This means that the careful pretreatment of the film will improve the cycle performances of the present layered composite. The coulombic efficiency in the charge/discharge cycle was practically 100%, except for the first cycle. The discharge potential was ranged from 4.0 to 3.0 V under this cycling condition.

For the PAn–Cl/PAn–PSS films, almost the same discharge capacity was obtained as those of PAn–ClO₄/PAn–PSS. In conclusion, it was proved that the present layered polymer composite films are promising positive electrode materials for the rechargeable lithium batteries with high energy densities. Detailed characteristics, e.g., dependencies of the cycle performances on the film composition, are now under investigation.

Acknowledgement

References

[1] K. Naoi, M. Lien and W.H. Smyrl, J. Electrochem. Soc., 138 (1991) 440.
[2] A. Shimizu, K. Yamataka and M. Kohno, Bull. Chem. Soc. Jpn., 61 (1988) 4401.
[3] T. Osaka, T. Momma and K. Nishimura, Chem. Lett., (1992) 1787.
[4] T. Momma, K. Nishimura, T. Osaka, A. Usui and S. Nakamura, in B.M. Barnett et al., (eds.), Proc. Symp. New Sealed Rechargeable Batteries and Supercapacitors, Honolulu, HI, USA, May 1993, Vol. 93-23, The Electrochemical Society, Pennington, NJ, USA, 1993, p. 199.
[5] M. Morita, R. Miyake, H. Tsutsumi and Y. Matsuda, Chem. Express, 5 (1990) 985.
[6] G. Bidan and B. Ehui, J. Chem. Soc., Chem. Commun., (1989) 1568.
[7] N. Li, J.Y. Lee and H. Ong, J. Appl. Electrochem., 22 (1992) 512.
[8] M. Morishita, S. Abe, A. Nojiri and K. Shinozaki, Trans. IEEE Jpn., 107-A (1987) 177.
[9] M. Morita, S. Miyazaki, H. Tanoue, M. Ishikawa and Y. Matsuda, J. Electrochem. Soc., 141 (1994) 1409.