

Preparation of poly(*N*-methylpyrrole) modified with pentathiepin rings and its application to positive active material for lithium secondary

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Abstract

Lithium secondary batteries with high energy density are key devices for portable electrical equipments. The specific capacity of metal oxide-based positive active materials is considerably lower than that of lithium metal. Organosulfur compounds, such as disulfide compounds are useful as a positive active material for lithium secondary cells. We prepared modified poly(*N*-methylpyrrole) (PMPy) with pentathiepin rings (S-PMPy) from PMPy and disulfur dichloride at room temperature. The S-PMPy electrode showed electrochemical responses in the organic electrolyte solution (mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) (1:1, v/v) containing 1 mol dm⁻³ LiClO₄). The maximum capacity of the test lithium secondary cell with the S-PMPy electrode was 14.8 A h kg⁻¹ (per kilogram of S-PMPy) and the average capacity was 11.5 A h kg⁻¹ (10 cycles) under the constant charge–discharge current condition at room temperature.

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1. Introduction

Lithium secondary batteries are key devices for portable electronic equipments, such as portable computer, cellular phone. The batteries with high energy density are indispensable electronic devices for improving portability of the apparatus. Organosulfur compounds with thiol or disulfide structure are candidates for positive active materials for high-energy density lithium secondary batteries [1–8]. For example, 2,5-dimercapto-1,3,4-thiadiazole (DMcT) is one of the most well-known organosulfur compounds whose theoretical charge density, 362 A h kg⁻¹, is two to three times higher than those of other groups of materials, such as metal oxide, conductive polymers.

Pentathiepins are seven-membered ring compounds containing a carbon–carbon double bond and five sulfur atoms. The first naturally occurring pentathiepins' examples, varacin, lissoclinotoxin A, and *N,N*-dimethyl-5-(methylthio)varacin, have strong antimicrobial and

antifungal activity and selectively inhibit protein kinase C, and varacin is highly toxic toward human colon cancer [9]. Pentathiepin compounds have polysulfide structure, which is electrochemically active [10]. For example, the electrochemical properties of 4,5-ethylenedithio-4,5-pentathiotetrafulvalene were investigated by cyclic voltammetry technique and the cyclic voltammogram measured in benzonitrile showed two pairs of reversible redox waves (the first and second redox potentials are 0.69 and 1.06 V versus Ag/AgCl, respectively) [10]. However, possibility of pentathiepin compounds as a cathodic material for battery systems has not been investigated.

In this paper we prepared 6-methylpentathiepino [6,7-*b*] indole [11] (see Fig. 1) and checked its electrochemical property in organic electrolyte solution by cyclic voltammetric technique for the first step of the investigation. We observed that the starting compound, 1-methylindole is less electrochemically active, however, 6-methylpentathiepino[6,7-*b*]indole is active. We concluded that modification of pentathiepin ring to electrochemically inactive compounds activates them.

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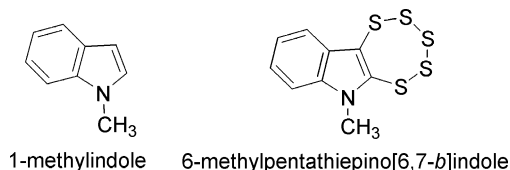


Fig. 1. Structure of 1-methylindole and 6-methylpentathiepine [6,7-*b*]indole.

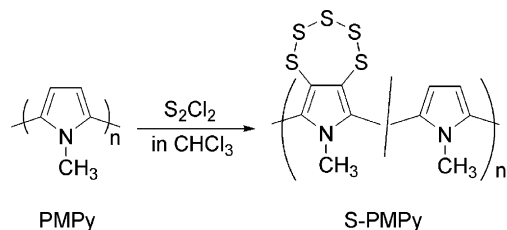


Fig. 2. Preparation route of poly(*N*-methylpyrrole) modified with pentathiepin rings (S-PMPy).

Furthermore, we presented the preparation of poly(*N*-methylpyrrole) (PMPy) modified with pentathiepin rings (Fig. 2) and its electrochemical behavior in organic electrolyte solution. We also constructed test cells with the compound as a positive active material and lithium as a negative active material. Charge–discharge performance of the cells was tested.

2. Experimental

2.1. Materials

All chemicals are used as received unless otherwise mentioned. 6-Methylpentathiepine [6,7-*b*]indole was prepared from 1-methylindole and disulfur dichloride following the literature [11]. Propylene carbonate (PC) and 1,2-dimethoxyethane (DME) (lithium battery grade, Mitsubishi Chemical Co.) was used for all electrochemical measurements.

Poly(*N*-methylpyrrole) (PMPy) was deposited on a Pt plate by electrochemical polymerization of *N*-methylpyrrole following the literature [12]. Modification of poly(*N*-methylpyrrole) was performed by dipping the Pt plate covered with PMPy into disulfur dichloride/chloroform solution at room temperature (20–25 °C) for 44 h (Fig. 2). Formation of pentathiepin rings in the *N*-methylpyrrole was confirmed by FTIR spectroscopic technique.

2.2. Measurements

Cyclic voltammograms for the electrodes in a conventional three-electrode configuration were recorded with an electrochemical measurement system. The measurements were performed at room temperature (20–25 °C). The electrolyte solution was 1 mol dm⁻³ LiClO₄/PC-DME (1:1, v/v). The electrode potential cited in this paper is referred to Li/Li⁺

reference electrode. All voltammograms were collected with a computer-controlled potentiostat-galvanostat (Z-3000, Hokuto). Cell structure for the charge–discharge cycling test was a similar cell configuration without the reference electrode for cyclic voltammetry measurements. Cycling performance of the cells was tested with a charge–discharge controller (HJ-101SM6, Hokuto) connected with a computer for data acquisition. All electrochemical measurements were performed in a glove box filled with argon (the dew point was –70 °C). FTIR spectra of the polymers were recorded with an FTIR spectrometer (FTIR-4200, Shimadzu).

3. Results and discussion

3.1. Electrochemical behavior of 1-methylindole and 6-methylpentathiepine [6,7-*b*]indole

Electrochemical behavior of organic compounds with pentathiepin structure has been reported by Ojima et al. [10], Nagahora et al. [13], and Kunugi et al. [14,15]. However, the electrochemical properties of 6-methylpentathiepine [6,7-*b*]indole (MPTI) have not been investigated. We compared the electrochemical responses between 1-methylindole (1-MI) and MPTI in organic electrolyte solution (1 mol dm⁻³ LiClO₄/PC-DME (1:1), v/v).

Fig. 3 shows the cyclic voltammograms of 1-MI and MPTI in 1 mol dm⁻³ LiClO₄/PC-DME (1:1, v/v) solution. We could not observe any obvious peaks in the voltammogram for 1-MI in the range between from 1 to 3.5 V versus Li/Li⁺. Malfoy and Reynaud [16] reported that oxidation potentials versus Ag/Ag⁺ were 0.80 V for 1-MI, and 0.65 V for 2- and 3-MIs. Their observations also support our observation. The electrochemical responses in the electrolyte with MPTI are presented in Fig. 3 as solid lines. In anodic scan the obvious peaks at 0.64, 0.89, 1.38, 2.00, 2.77, and 3.25 V. In cathodic scan the peaks at 2.30, 1.50, 0.67, and 0.32 V. Studies on variation of

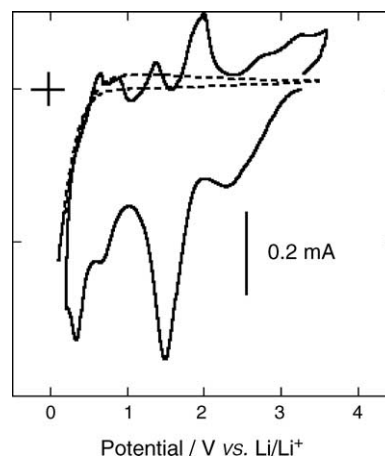


Fig. 3. Cyclic voltammograms of 1-methylindole (dotted line) and 6-methylpentathiepine [6,7-*b*] indole (solid line) in 1 mol dm⁻³ LiClO₄/PC-DME (1:1, v/v). Scan rate 5 mV s⁻¹.

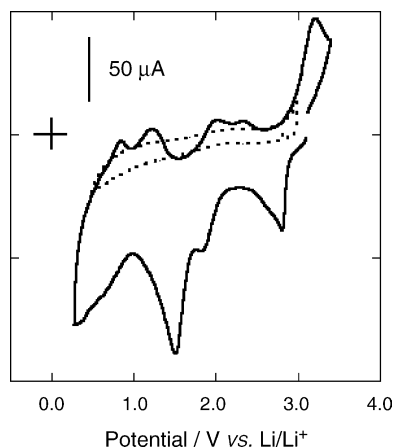


Fig. 4. Cyclic voltammograms of PMPy electrode (dotted line) and S-PMPy electrode (solid line) in $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$ (1:1, v/v). Scan rate 5 mV s^{-1} .

the scanning potential range in the voltammetry indicate that the anodic peak at 2.0 V and the cathodic one at 1.5 V, and the anodic one at 0.64–0.89 V and cathodic one at 0.32–0.67 V are two pairs of reversible redox waves. Modification of 1-MI with pentathiepin ring changes the electrochemical responses of 1-MI. Introducing pentathiepin structure into an electrochemically inactive compound induces electrochemically activation of the compound. We applied this concept to modification of poly(*N*-methylpyrrole) electrode in the next section.

3.2. Electrochemical behavior of poly(*N*-methylpyrrole) and poly(*N*-methylpyrrole) with pentathiepin structure

Modification reactions of conjugated compounds with pentathiepin rings have been investigated by many organic chemists [9]. Treatment of a conjugated compound, such as indoles and pyrroles with disulfur dichloride (S_2Cl_2) is one of the methods for introducing pentathiepin rings to the compounds under mild condition (at room temperature) [11]. We prepared a poly(*N*-methylpyrrole) film on a Pt electrode by electrochemical oxidation of *N*-methylpyrrole [12]. The resulted polymer film on the Pt electrode was treated with $\text{S}_2\text{Cl}_2/\text{chloroform}$ solution at room temperature (20–25 °C) for 44 h. FTIR spectrum of the processed poly(*N*-methylpyrrole) suggests that the pentathiepin structure is introduced into the poly(*N*-methylpyrrole) film on the Pt plate.

Fig. 4 shows the cyclic voltammograms of PMPy and S-PMPy electrodes in organic electrolyte solution. We observed current peaks at 0.87, 1.22, 2.00, 2.34, and 3.20 V in anodic scan and at 1.52, 1.86, and 2.81 V in cathodic scan with the S-PMPy electrode. No obvious current peak was observed in the PMPy electrode in this potential scanning range. This result suggests that introducing pentathiepin rings to PMPy activates PMPy. Comparing the voltammogram of MPTI (solid line in Fig. 3) to that of S-PMPy (solid line in Fig. 4) similar electrochemical responses were observed. This also indicates

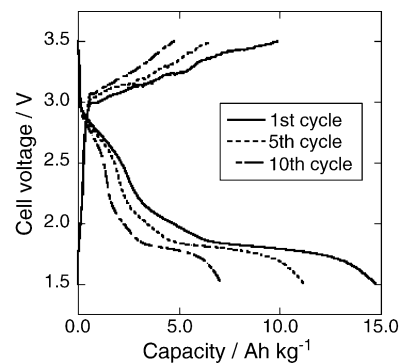


Fig. 5. Charge–discharge curves of $\text{Li}|1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$ (1:1, v/v)|S-PMPy test cell. Charge–discharge current is $5 \mu\text{A cm}^{-2}$ (per square centimeter of apparent surface area of Pt electrode). Solid line is 1st, dotted line is 5th, and dashed line is 10th cycle's charge–discharge curve.

that the PMPy film was modified with pentathiepin rings by the treatment with S_2Cl_2 at room temperature.

3.3. Charge–discharge behavior of test lithium battery with poly(*N*-methylpyrrole) with pentathiepin structure

Charge–discharge performance of the test cell, $\text{Li}|1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$ (1:1, v/v)|S-PMPy electrode, was tested under constant current condition $5 \mu\text{A cm}^{-2}$ (per square centimeter of apparent surface area of the S-PMPy electrode), cut off voltage 1.5 and 3.5 V. Fig. 5 shows the charge–discharge profiles of the test cell at 1st, 5th, and 10th cycle. At 1st cycle potential plateau at about 1.6–1.8 V was observed. The potential plateau is attributed to the current peak on the cyclic voltammogram on Fig. 4. Under continuous charge–discharge cycling condition the capacity of the cell decreased.

Fig. 6 shows the variation of the capacity of the cell with cycle number. Maximum capacity of the cell was 14.8 Ah kg^{-1} (per kilogram of S-PMPy on the electrode). Average capacity of the cell was 11.5 Ah kg^{-1} (over 10 cycles). The cell performance is not enough for practical use of the material. However, we show that the new positive active

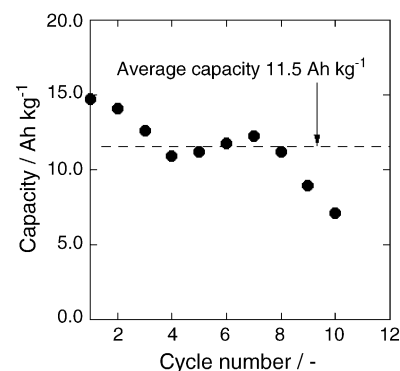


Fig. 6. Variation of discharge capacity of $\text{Li}|1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$ (1:1, v/v)|S-PMPy test cell. Charge–discharge current is $5 \mu\text{A cm}^{-2}$ (per square centimeter of apparent surface area of Pt electrode).

material can be prepared by the simple technique, dipping the PMPy into $S_2Cl_2/CHCl_3$ solution at room temperature.

4. Conclusions

Electrochemically inactive compounds such as 1-methylindole, poly(*N*-methylpyrrole) were activated by modification with pentathiepin structure. The modified compounds, 6-methylpentathiepin [6,7-*b*]indole (MPTI), poly(*N*-methylpyrrole) with pentathiepin (S-PMPy) showed many current peaks from 0.5 to 3.5 V versus Li/Li⁺.

The test lithium secondary battery, Li|1 mol dm⁻³ LiClO₄/PC-DME (1:1, v/v)|S-PMPy electrode, was constructed and its charge–discharge performance was also investigated. Maximum capacity of the cell was 14.8 A h kg⁻¹ (per kilogram of S-PMPy on the electrode). Average capacity of the cell was 11.5 A h kg⁻¹ (over 10 cycles).

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