

# New type polyamides containing disulfide bonds for positive active material of lithium secondary batteries

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## Abstract

Various polyamides containing a disulfide bond in their main chain were prepared by condensation of a diacid, 3,3'-dithiodipropionic acid (P), 6,6'-dithiodimicotinic acid (N), or 2,2'-dithiodibenzoic acid (B) and a diamine, alkyldiamine (I, II, III, and IV:  $\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2$ ,  $n=4, 6, 8,$  and  $12$ ) or cystamine, V:  $\text{NH}_2-(\text{CH}_2)_2-\text{S}-\text{S}-(\text{CH}_2)_2-\text{NH}_2$ . Polyamides P-I, P-II, P-III, P-IV, and P-V were insoluble common organic solvents, but soluble in formic acid or trifluoroacetic acid. Polyamides containing N or B as the acid moiety, i.e. aromatic polyamides, were soluble in *N,N'*-dimethylformamide or dimethyl sulfoxide. The electrochemical behavior of P-II electrode in the organic electrolytes, such as propylene carbonate (PC), PC–1,2-dimethoxyethane (DME) mixture, ethylene carbonate (EC)–DME mixture, which are used as the electrolytes for common lithium batteries was investigated. In the mixed electrolyte, PC–DME (1:1, by volume) a good electrochemical response of P-II electrode based on the redox of disulfide bonds in the polymer was observed. Charge/discharge cycling tests of L1/P-II cells were also performed. At the first discharge, the net capacity of the cell was  $97.5 \text{ Ah kg}^{-1}$  (this value was calculated from the weight of loaded P-II on the electrode). Utilization of P-II was 53%. Cell capacity versus cycle number was also investigated. © 1997 Elsevier Science S.A.

**Keywords:** Disulfides; Positive active materials; Polyamides; Secondary batteries

## 1. Introduction

Various organic compounds containing disulfide bonds, organosulfur compounds, are one of the most attractive and interesting candidates' groups of positive active materials for high energy storage secondary lithium batteries [1–11]. Their theoretical capacity is very high, for example, the theoretical capacity of 2,5-dimercapto-1,3,4-thiadiazole is about  $362 \text{ Ah kg}^{-1}$ . Furthermore, the redox reaction of organosulfur compounds,  $\text{R}-\text{S}-\text{S}-\text{R} + 2e^- = 2(\text{RS}^-)$ , is usually reversible, where R represents an organic moiety. The reactivity, solubility, and electrical capacity of the organodisulfides depend on the structure of R. The design of the R moiety is a key point for the application of these compounds in the active material for secondary batteries. Previously, we reported the preparation of polyamides containing disulfide bonds and their electrochemical behavior in acetonitrile electrolyte solution [10,11]. All polyamides were prepared by condensation of an acid dichloride and a diamine with the interfacial polymerization technique. We produced various polyamides containing a disulfide bond and different R moieties by selecting a pair of diacid and diamine. Fig. 1 shows

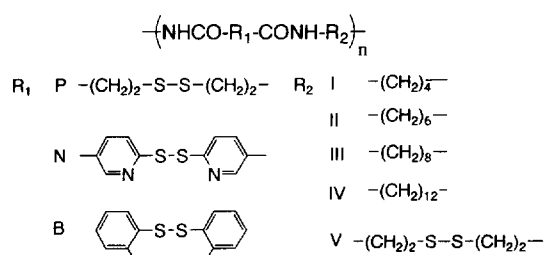


Fig. 1 Structure of various polyamides containing a disulfide bond.

Table 1  
Theoretical capacity ( $\text{Ah kg}^{-1}$ ) of polyamides containing disulfide bond

Diacid <sup>a</sup>	Diamine <sup>a</sup>				
	I	II	III	IV	V
P	204	185	168	143	328
N	148	138	129	113	253
B	150	139	129	114	254

<sup>a</sup> Detail structures are presented in Fig. 1.

structures of the polyamides; their theoretical electric capacity was listed in Table 1. Acids used for preparation of polyamides were 3,3'-dithiodipropionic acid (P), 6,6'-

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dithiodinicotinic acid (N), or 2,2'-dithiodibenzoic acid (B). Diamine was alkyldiamine (I–IV:  $\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2$ ,  $n=4, 6, 8, 12$ ), or cystamine V:  $\text{NH}_2-(\text{CH}_2)_2-\text{S}-\text{S}-(\text{CH}_2)_2-\text{NH}_2$ . All polyamides were prepared by condensation of the corresponding acid dichloride and the corresponding diamine with the interfacial polymerization technique.

In this study, we report the redox behavior of the polymers in organic electrolyte solutions, especially polyamide P-II, and the charge/discharge behavior of the model, Li/P-II cell.

## 2. Experimental

### 2.1. Materials

3,3'-dithiodipropionic acid (Aldrich), 6,6'-dithiodinicotinic acid (Aldrich), 2,2'-dithiodibenzoic acid (Ishizu), thionyl chloride (Ishizu), various alkyldiamines, ( $\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2$ ,  $n=4, 6, 8, 12$ , Ishizu), cystamine (Ishizu), and acetonitrile (HPLC grade, Ishizu) were used as received. The solvents for electrolyte solution were propylene carbonate (PC), a 1:1 (by volume) mixture of PC and 1,2-dimethoxyethane (DME), ethylene carbonate (EC), and a 1:1 (by volume) mixture of EC and DME, which were used as received (Mitsubishi Petrochemical, battery grade). Lithium perchlorate trihydrate (Ishizu) was dried at 150 °C for 24 h to remove hydrated water. Graphite powder (Wako) was also used as received.

### 2.2. Preparation of polyamides

Polyamides were prepared by condensation of the corresponding acid and diamine with the interfacial polymerization technique. The typical preparation procedure was as follows: a mixture of 2.5 g of 3,3'-dithiodipropionic acid (12 mmol) and 10.0 ml of excess thionyl chloride was heated under reflux for 90 min. After cooling the mixture to room temperature, excess thionyl chloride was removed by using a rotary evaporator. The oily acid chloride was dissolved with 100 ml of  $\text{CCl}_4$  or  $\text{CHCl}_3$ . Corresponding diamine (12 mmol) was dissolved into a sodium hydroxide aqueous solution (1.92 g, 48 mmol/100 ml). The diamine aqueous solution was gradually added to the acid chloride/ $\text{CCl}_4$  or  $\text{CHCl}_3$  solution. Polyamide was formed at the  $\text{H}_2\text{O}/\text{CCl}_4$  or  $\text{CHCl}_3$  interface. The resulted polymer was collected, washed with ethanol, water, and ethanol, and dried under vacuum over 24 h at room temperature. The structure of polyamides was confirmed by IR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR measurements.

### 2.3. Electrochemical measurements

Electrochemical measurements for polyamides were performed with a conventional three-electrode cell. The working electrode was a carbon-paste electrode [10–15]. The configuration of the working electrode was reported in our previous paper [10]. Prepared polyamide electrode is the mixed carbon-paste electrode. A mixture of polyamide, graphite powder, and a small amount of the electrolyte solution was blended in a mortar and the paste was loaded on the glassy

carbon electrode: the top of the electrode was covered with a polypropylene separator sheet to hold the paste on the electrode. The electrode is called polyamide electrode, for example, P-II electrode. Usual paste for polyamide electrode was prepared by mixing polyamide and graphite in a weight ratio of 1:1. Unless otherwise stated, the concentration of  $\text{LiClO}_4$  was  $0.1 \text{ mol dm}^{-3}$ . All solutions for electrochemical measurements were degassed with argon for 30 min prior to use. In cyclic voltammetry measurements a potentiostat-galvanostat (HA-301, Hokuto), a function generator (HB-104, Hokuto), and an  $x$ - $y$  recorder (WX-1100, Graphtec) were used. The electrode potentials cited in this paper are referred to an  $\text{Li}/\text{Li}^+$  electrode.

Cycling tests of the model cell were performed with a charge/discharge controller (HJ-201, Hokuto Denko) and an  $x$ - $t$  recorder (Type 3057, Yokokawa).

## 3. Results and discussion

### 3.1. Structure and properties of polyamides containing disulfide bond

The structure of polyamides are presented in Fig. 1.

All polymers have disulfide bonds in their main chain. The distance from one disulfide bond to the next one is different in polyamides studied. Among the polyamides, the distance in P-II is the shortest and in polyamide P-IV the longest. All polyamides are colorless and odorless powders, and stable in air. The polyamides containing P as the acid moiety, P-I, P-II, P-III, P-IV, and P-V, are insoluble in usual organic solvents, such as acetonitrile, alcohol, acetone, and ether. They are soluble in formic acid and trifluoroacetic acid. The aromatic polyamides containing N or B as acid moiety are soluble in  $N,N'$ -dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The structure of polyamides was confirmed by IR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy. For example, the IR spectrum of P-II showed bands at  $1640 \text{ cm}^{-1}$  and  $1550 \text{ cm}^{-1}$  which are attributed to the amide I and amide II bands, respectively [16]. NMR results for the polyamides also supported the structure as presented in Fig. 1.

### 3.2. Electrochemical behavior of polyamides containing disulfide bond in organic electrolyte

Fig. 2 shows the cyclic voltammograms for a P-II electrode in various organic electrolyte solutions containing  $0.1 \text{ mol dm}^{-3}$   $\text{LiClO}_4$ . The mixing weight ratio of P-II and graphite was 1:1. The counter electrode was a lithium foil, and the reference electrode was a lithium tip ( $\text{Li}/\text{Li}^+$ ). The electrode potentials cited in this section are referred to the  $\text{Li}/\text{Li}^+$  electrode.

As shown in Fig. 2(a), the increase in cathodic current was observed from 2.0 to 1.3 V in the first negative scan. In the positive scan the anodic peak at 2.9 V was observed. The increase in cathodic current is due to the reduction of disulfide bonds in the polyamide and the anodic peak arises from the oxidation of thiol or thiolate to disulfide. However, the quan-

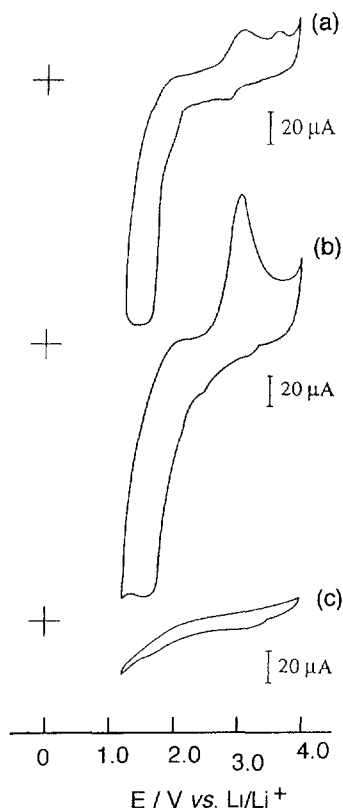


Fig. 2. Cyclic voltammograms of P-II electrode in various organic electrolytes containing  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ . Scan rate  $0.5 \text{ mV s}^{-1}$ . Mixing ratio of P-II and graphite is 1:1, by weight. Counter electrode: Li foil; reference electrode: Li tips ( $\text{Li/Li}^+$ ). (a) PC, (b) PC-DME (1:1, by volume), and (c) EC-DME (1:1, by volume)

tivity of electricity estimated from the anodic peak area is smaller than that from the cathodic area. This suggests that P-II is not preferable to use as the positive material in the PC electrolyte. Fig. 2(c) shows the voltammogram of the P-II electrode in EC-DME (1:1, by volume) electrolyte. In this electrolyte solution, any obvious current peak or increase in current was not observed. The EC-DME mixed electrolyte solution interferes the redox of disulfide in P-II. Fig. 2(b) shows the voltammogram of the P-II electrode in PC-DME (1:1, by volume) electrolyte. The increase in cathodic current in the negative-going scan was observed to be similar as in the PC electrolyte. An anodic peak at 2.9 V in the positive scan was observed. The anodic peak current was larger than that in the PC electrolyte. Therefore, PC-DME (1:1, by volume) mixed electrolyte is suitable as a electrolyte for the P-II electrode. The reason is not clear. It may be concerned with the stability of the thiolate anion in the electrolyte and/or suppression of side reactions of P-II and its derivatives in the electrolyte.

### 3.3. Discharge/charge behavior of Li/P-II model cell

The model cell, Li/P-II cell, was fabricated and the cycling performance of the cell was demonstrated. The configuration of the positive electrode and the cell in the model cell was

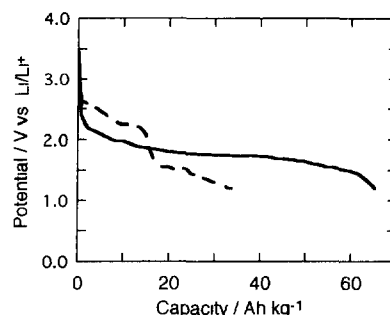


Fig. 3. First discharge curves of an (—) Li/P-II cell and (- - -) Li/graphite cell. Electrolyte  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$  (1:1, by volume). Electrodes: P-II electrode, P-II 46.5 mg and graphite 46.5 mg, graphite electrode, graphite 47.0 mg. Electrolyte:  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$  (1:1, by volume). Current density:  $500 \mu\text{A g}^{-1}$  ( $5.3 \times 10^{-3} \text{ C}$  in the case of the Li/P-II cell). Cutoff voltage 1.2 V.

same as that for the cyclic voltammetric measurements. The potential was referred to the reference electrode.

Fig. 3 shows the first discharge curves of the Li/P-II cell and Li/graphite cell. The Li/graphite cell was used to estimate the net capacity of the P-II electrode. The current density was  $500 \mu\text{A g}^{-1}$  per gram of positive electrode, and the cutoff voltage was 1.2 V. The potential of the Li/P-II cell decreased from 4.0 to 2.4 V, rapidly at the initial stage of the discharge process. After this process, the potential of the cell decreased gradually. The first discharge capacity of the Li/P-II cell was  $66.0 \text{ Ah kg}^{-1}$  (per kilogram of P-II electrode, the mixed ratio of P-II and graphite is 1:1, by weight). The discharge capacity of the Li/graphite cell was  $34.5 \text{ Ah kg}^{-1}$  (per kilogram of graphite electrode). Thus P-II polymer in the cell acted as a positive active material. The net capacity of the P-II electrode based on the weight of P-II was  $97.5 \text{ Ah kg}^{-1}$ . The theoretical capacity of the polyamides was  $185 \text{ Ah kg}^{-1}$  (see Table 1). The P-II utilization was 53%.

Fig. 4 shows the variation of discharge capacity for the Li/P-II and Li/graphite cells versus cycle number.

The capacity of the Li/P-II cell decreased gradually with the cycle number. However, the capacity of Li/graphite cell also decreased to about  $2\text{--}3 \text{ Ah kg}^{-1}$ . The further observed cell capacity of the Li/P-II cell after the first discharge was

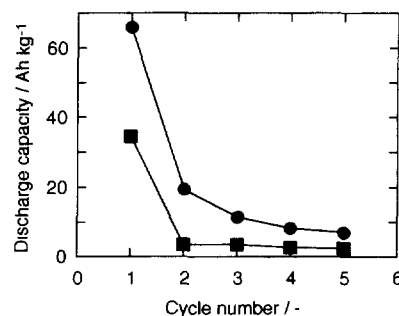


Fig. 4. Variation of discharge capacities (per kilogram of loaded electrode material paste) for (●) Li/P-II cell and (■) Li/graphite cell with cycle number. Electrode: P-II electrode, P-II 46.5 mg; graphite 46.5 mg, graphite electrode, graphite 47.0 mg. Electrolyte:  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$  (1:1, by volume). Current density:  $500 \mu\text{A g}^{-1}$  (per gram of polyamide and graphite). Potential range: 1.2–4.0 V (vs.  $\text{Li/Li}^+$ ).

based on the redox reaction of P-II. Optimization of various conditions, such as the configuration of the electrode, the mixing ratio of conductive material and P-II, current density, should be performed in order to apply P-II and other polyamide materials in practical lithium batteries.

Other polyamides have been prepared and investigation of their electrochemical behavior is now in progress.

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