

Electrochemical behavior of polyamides with cyclic disulfide structure and their application to positive active material for lithium secondary battery

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Abstract

Polyamides (DTA-I, DTA-II, and DTA-III) containing cyclic disulfide structure were prepared by condensation between 1,2-dithiane-3,6-dicarboxylic acid (DTA) and alkyl diamine, $\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2$ (DTA-I; $n=4$, DTA-II; $n=6$, DTA-III; $n=8$) and their application to positive active material for lithium secondary batteries was investigated. Cyclic voltammetry (CV) measurements under slow sweep rate (0.5 mV s^{-1}) with a carbon paste electrode containing the polyamide (DTA-I, DTA-II, or DTA-III) were performed. The results indicated that the polyamides were electroactive in the organic electrolyte solution (propylene carbonate (PC)-1,2-dimethoxyethane (DME), 1:1 by volume containing lithium salt, such as LiClO_4). The responses based on the redox of the disulfide bonds in the polyamide were observed.

Test cells, Li/PC-DME (1:1. by volume) with $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ /the polyamide cathode, were constructed and their performance was tested under constant current charge/discharge condition. The average capacity of the test cells with the DTA-III cathode was 64.3 Ah kg^{-1} of cathode (135 Wh kg^{-1} of cathode, capacity (Ah kg^{-1}) of the cathode \times average cell voltage (2.10 V)). Performance of the cell with linear polyamide containing disulfide bond ($-\text{CO}-(\text{CH}_2)_2-\text{S}-\text{S}-(\text{CH}_2)_2-\text{CONH}-(\text{CH}_2)_8-\text{NH}-$, GTA-III) was also investigated and the average capacity was 56.8 Ah kg^{-1} of cathode (100 Wh kg^{-1} of cathode, capacity (Ah kg^{-1}) of the cathode \times average cell voltage (1.76 V)). Cycle efficiency of the test cell with the DTA-III cathode was higher than that with the GTA-III cathode. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Disulfide; Polyamide; Cathode active material; Lithium battery; Lithium secondary battery

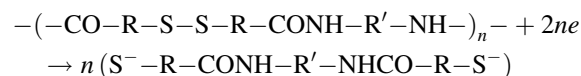
1. Introduction

A high-power secondary and weightless battery is one of the most important devices for lightening potable electrical equipment. Organosulfur compounds, such as 2,5-dimercapto-1,3,4-thiadiazole (DMcT), which have polymerizable sulfur groups, are one of the most promising candidates of positive active materials for a high-energy storage secondary battery [1,2]. Electrochemical behavior and application of DMcT to cathode active material for lithium secondary batteries have been investigated. Disadvantage point of DMcT is its solubility in typical organic solvent, such as propylene carbonate (PC). Thus, solid- or gel-polymer electrolytes have been used as an electrolyte for the cell with DMcT cathode [3,4].

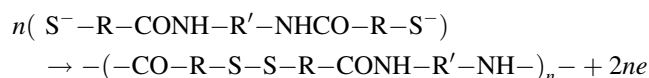
We have been preparing various linear polyamides containing disulfide bonds and diamine in their main chains

$[-(\text{CO}-\text{R}-\text{S}-\text{S}-\text{R}-\text{CONH}-\text{R}'-\text{NH}-)]_n-$. Their electrochemical behavior and the performance of the test cells with the cathodes have been reported [5–9].

Discharge process (reduction):



Charge process (oxidation):



The thiolate anions ($\text{S}^- - \text{R}-\text{CONH}-\text{R}'-\text{NHCO}-\text{R}-\text{S}^-$) produced by reduction of the polyamide were not soluble in organic electrolytes [5]. However, decrease in capacity for the polyamide cathode was observed and the phenomenon should be caused by cleavage of the main chain containing disulfide bonds and difficulty of re-production of disulfide bonds by their steric hindrance.

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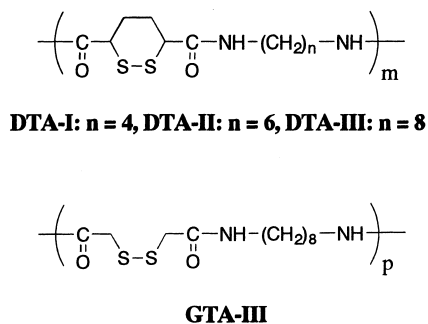


Fig. 1. Structures of polyamides, DTA-I, DTA-II, DTA-III, and GTA-III.

We report here preparation of the polyamides containing cyclic disulfide structure (DTA-I, DTA-II, and DTA-III, Fig. 1) and their application to positive active material for a lithium secondary battery. The polyamides were prepared by condensation between 1,2-dithiane-3,6-dicarboxylic acid (DTA) and alkyldiamine.

When the disulfide bonds in the DTA-based polymer are cleaved under reduction (discharge) process, the polymer main chains are not divided. We investigated electrochemical properties of the polyamides in organic electrolytes. Furthermore, we constructed the test cells containing the polyamide as the cathode active material for secondary lithium batteries and their performance was tested. The linear polyamide (Dithiodigrycolic acid (GTA)-III, in Fig. 1) was also prepared and performance of the cell with the GTA-III electrode was compared with that of the cell with the DTA-III cathode.

2. Experimental

2.1. Preparation of polyamides

Dicarboxylic acid, 1,2-dithiane-3,6-dicarboxylic acid (DTA), was prepared from adipic acid following the literature [10]. Alkyldiamines, $\text{NH}_2\text{---}(\text{CH}_2)_n\text{---NH}_2$ (DTA-I; $n=4$, DTA-II; $n=6$, DTA-III; $n=8$) were purchased from Ishizu and used without further purification. Dithiodigrycolic acid (GTA) was also purchased from Ishizu and used for preparation of linear polyamide (GTA-III).

Polyamides (DTA-I, DTA-II, and DTA-III) were prepared by condensation between 1,2-dithiane-3,6-dicarboxylic acid and alkyldiamine. Typical preparation procedure of the polyamides is as follows.

A 0.5 g (2.4 mmol) of diacid (1,2-dithiane-3,6-dicarboxylic acid or dithiodigrycolic acid) was dissolved into 5 ml of excess thionyl chloride under Ar gas. The mixture was heated under reflux for 2 h. After cooling the mixture to room temperature, unreacted thionyl chloride was removed using a rotary evaporator. The oily acid chloride was dissolved with 10 ml of tetrachloromethane (CCl_4) or chloroform (CHCl_3). The corresponding diamine (2.4 mmol) was dissolved into a sodium hydroxide aqueous solution (0.2 g,

5 mmol/10 ml). The diamine aqueous solution was gradually added to the acid chloride- CCl_4 or CHCl_3 solution. Polyamide was formed at the water/organic layer interface. The resulting polymer was collected, washed with water and freeze-dried. Linear polyamide, GTA-III, was prepared from dithiodigrycolic acid and alkyldiamine under the similar procedure. The structure of the polyamides, DTA-I, DTA-II, DTA-III, and GTA-III, was confirmed by FTIR and ^{13}C CP/MAS solid state NMR measurements.

2.2. Measurements

Detailed configuration of the carbon paste electrode for this study was described in our previous paper [5]. A mixture of polyamide, acetylene black, and a small amount of the electrolyte solution were blended with a mortar and pestle, and the paste was loaded on a glassy carbon current collector. Typical loading levels of polyamide on the electrode was 2:8 (polymer:acetylene black) by weight. Cyclic voltammograms for the carbon paste electrodes were recorded with a potentiogalvanostat (HA-301, Hokuto), a function generator (HB-104, Hokuto), and an X-Y recorder (WX-1100, Graphtec). The measurements were performed at room temperature (20–25°C). All the electrode potential cited in this paper are referred to Li/Li^+ reference electrode.

Cell structure for the test battery was a similar cell configuration without a reference electrode for cyclic voltammetry measurements. Cycling performance of the cells were tested with a charge/discharge controller (HJ-101SM6, Hokuto) connected with a computer for data acquisition.

FTIR spectra of the polymers were recorded with an FTIR spectrometer (FTIR-4200, Shimadzu). ^{13}C CP/MAS NMR spectra of the polymers were measured with an NMR spectrometer with a magic angle spinning probe (CMX-300 Infinity, Chemagnetic). The observed peaks were referred to the peak position (δ : 17.35 ppm from tetramethylsilane (TMS)) of methyl carbon in hexamethylbenzene.

3. Results and discussion

3.1. Structures of polyamides

Structures of the polyamides (DTA-I, DTA-II, DTA-III, and GTA-III) were confirmed by FTIR and ^{13}C CP/MAS NMR measurements of them. The peaks attributed to amide bonds (amide I and amide II bonds) in the polyamides were observed at 1650 cm^{-1} (DTA-I, DTA-II, GTA-III), or 1640 cm^{-1} (DTA-III) and 1580 cm^{-1} (DTA-I), 1540 cm^{-1} (DTA-II), 1530 cm^{-1} (DTA-III), or 1560 cm^{-1} (GTA-III).

In their NMR spectra the peaks at 174–171 ppm ($-\text{CO}-$), 53–52 ppm ($-\text{NH}-\text{CH}_2-$), 40–42 ppm ($-\text{CH}-\text{S}-$), and 29–18 ppm (broad peak, methylene carbons) were also observed. Both results of IR and NMR measurements of the polymers suggested that their structures were same as shown in Fig. 1.

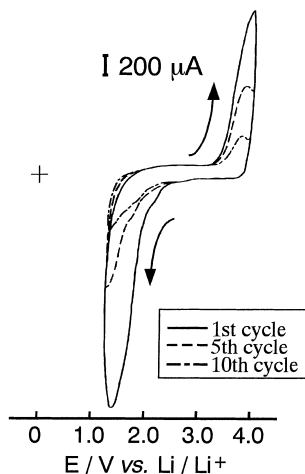


Fig. 2. Cyclic voltammograms for DTA paste electrode in PC-DME (1:1, by volume) electrolyte containing 1 mol dm^{-3} LiClO_4 . Scan rate at 0.5 mV s^{-1} .

3.2. Redox behavior of DTA and polyamides containing cyclic disulfide

Visco's group has reported electrochemical properties of various organosulfur compounds in organic electrolyte solution [11–13]. However, electrochemical behavior of cyclic disulfides such as DTA has not been reported. We studied the electrochemical behavior of DTA in an organic electrolyte solution. Fig. 2 shows the voltammograms of DTA-paste electrode in PC-DME electrolyte containing 1 mol dm^{-3} LiClO_4 at a slow scan rate of 0.5 mV s^{-1} .

Both cathodic peak at 1.4 V and anodic peak at 3.8 V were observed. Appearance of both peaks indicates disulfide bonds in the acid are electroactive in the electrolyte solution. However, redox response of the paste electrode disappeared with over 20 potential cycles. This phenomenon is based on the solubility of reduced DTA and its migration from the paste electrode to the electrolyte solution.

Fig. 3 shows the voltammograms for the DTA-III paste electrode in PC-DME containing 1 mol dm^{-3} LiClO_4 . Both cathodic and anodic peaks corresponding to redox response of disulfide in polyamide were observed at 1.5 and 3.6 V , respectively. The electrochemical behavior of the DTA-III electrode almost agrees with that of the DTA-I (see Figs. 2 and 3). The potential of cathodic peak shifted slightly to positive and that of anodic one shifted slightly to negative. This suggests that formation of amide bonds on DTA unit affect the redox potential of disulfide in DTA unit. Liu et al. reported that the redox potential and the redox reaction rate of disulfide in organic compounds were strong function of compound structure, especially, the atoms in the α and β positions adjacent to the sulfur atoms [14].

Electrochemical responses for DTA-I and DTA-II electrodes were almost similar to that for the DTA-III electrode. Theoretical capacity of the polyamides is 206 Ah kg^{-1} for DTA-I, 186 Ah kg^{-1} for DTA-II, and 169 Ah kg^{-1} for

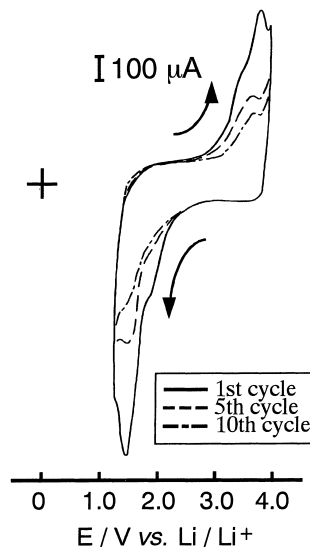


Fig. 3. Cyclic voltammograms for DTA-III paste electrode in PC-DME (1:1, by volume) electrolyte containing 1 mol dm^{-3} LiClO_4 . Scan rate at 0.5 mV s^{-1} .

DTA-III, calculated from two-electron transfer redox reaction of the disulfide bond on DTA structure. Utilization of the polyamide electrodes estimated from peak area of the voltammograms is 18.3% for DTA-I, 40.6% for DTA-II, and 44.6% for DTA-III electrodes.

Polyamide with linear disulfide structure (GTA-III) was also prepared and its electrochemical property was investigated. Fig. 4 shows the cyclic voltammograms for the GTA-III paste electrode under comparable condition of DTA-based polyamide electrodes. At 1st cycle, both peaks at 1.5 and 3.2 V were observed. The peak current decreased with the potential cycling processes. Capacity of the GTA-III electrode was 105 Ah kg^{-1} at 1st cycle and 20 Ah kg^{-1} at

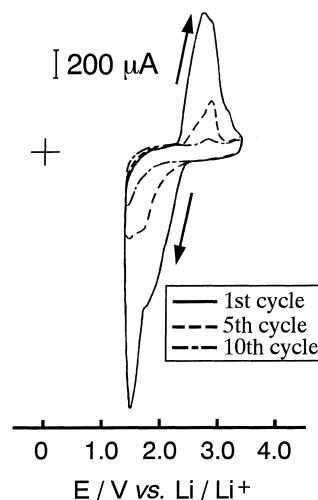


Fig. 4. Cyclic voltammograms for GTA-III paste electrode in PC-DME (1:1, by volume) electrolyte containing 1 mol dm^{-3} LiClO_4 . Scan rate at 0.5 mV s^{-1} .

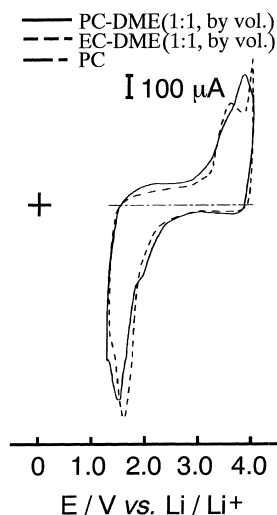


Fig. 5. Cyclic voltammograms for DTA-III paste electrode in an organic electrolyte (PC, PC-DME(1:1, by volume), or EC-DME(1:1, by volume)) containing $1 \text{ mol dm}^{-3} \text{ LiClO}_4$. Scan rate at 0.5 mV s^{-1} .

10th cycle. While, capacity of the DTA-III electrode was 76 Ah kg^{-1} at 1st cycle and 37 Ah kg^{-1} at 10th cycle. The decreasing rate of capacity for GTA-III electrode was higher than that of DTA-III electrode. When the disulfide bonds in the polymer chain are cleaved under reduction process, GTA-III chains are divided while DTA-III chains are not. The cleavage of the polymer chains with electrochemical reduction process may be closely related with the degree of decrease in capacity.

3.3. Effect of solvent and salt for electrolyte on redox behavior of polyamides

Electrochemical behavior of the polyamides containing disulfide bonds in various electrolytes was also investigated.

Fig. 5 shows the cyclic voltammograms for the DTA-III electrodes in various electrolytes prepared from PC, PC-DME, or EC-DME containing $1 \text{ mol dm}^{-3} \text{ LiClO}_4$. In PC/ LiClO_4 electrolyte, no electrochemical responses of the DTA-III electrode were observed, which suggests that the DTA-III electrode was inactive in PC electrolyte. This reason is not clear yet. However, in PC-DME/ LiClO_4 electrolyte, electrochemical responses of the DTA-III electrode were observed. Furthermore, in EC-DME electrolyte, the DTA-III electrode was electrochemically active and similar responses in PC-DME system were observed. We selected PC-DME mixed solvent system as a solvent for construction of the test cells. Choosing lithium salt for the electrolyte was also performed. Electrochemical responses for the DTA-III electrodes in electrolyte containing various lithium salts were accomplished with cyclic voltammetry technique. Shapes of the voltammograms for DTA-III electrodes were similar irrespective of the salts. However, lithium salt in the electrolyte affected the capacities of the DTA-III electrodes estimated from peak area of the voltammogram.

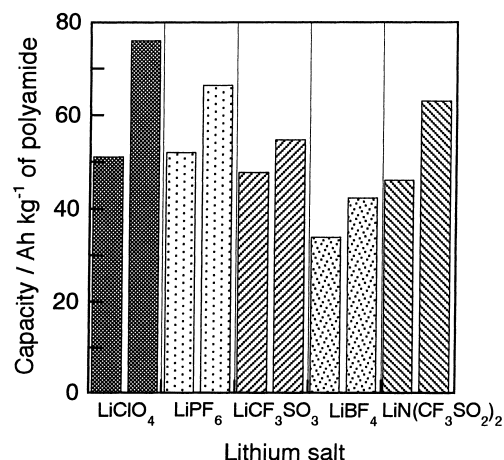


Fig. 6. Variation of average (left bar) and maximum (right bar) capacities for DTA-III electrode in PC-DME (1:1, by volume) containing lithium salts of LiClO_4 , LiPF_6 , LiCF_3SO_3 , LiBF_4 , or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$.

Fig. 6 shows average and maximum capacities for the DTA-III electrodes in PC-DME electrolytes containing lithium salts of LiClO_4 , LiBF_4 , LiPF_6 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. Maximum capacity of the DTA-III electrode was 76 Ah kg^{-1} in LiClO_4 electrolyte, 66 Ah kg^{-1} in LiPF_6 , 63 Ah kg^{-1} in $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, 54 Ah kg^{-1} in LiCF_3SO_3 , and 42 Ah kg^{-1} in LiBF_4 . Electrochemical stability of anion and/or conductivity of the electrolyte may be closely related with the salt dependence of capacity. Conductance between a current collector and polyamide and acetylene black particles affects the amount of active material in a paste electrode on redox cycling. Conductivity of PC-DME based electrolyte containing 1 mol dm^{-3} of a lithium salt is LiPF_6 (8.8 mS cm^{-1}), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (7.1 mS cm^{-1}), LiClO_4 (5.7 mS cm^{-1}), LiBF_4 (3.3 mS cm^{-1}), and LiCF_3SO_3 (1.7 mS cm^{-1}) [15]. Tendency of capacity dependence on variation of lithium salt is partially compatible with that of conductivity for the electrolyte solution. We selected PC-DME electrolyte containing LiClO_4 for electrolyte of test cells.

3.4. Charge/discharge behavior of Li/polyamide cell under various conditions

Based on the results described above sections, test cells with the DTA-III cathode and lithium anode with PC-DME electrolyte containing LiClO_4 were constructed and charge/discharge tests of them were performed. Fig. 7 shows the first charge/discharge profile for Li/polyamide (DTA-III) cells under 5 mA g^{-1} of polyamide. The potential profiles of the test cell with linear polyamide (GTA-III) cathode are also plotted in Fig. 7.

Average discharge voltage of the Li/DTA-III cell and the Li/GTA-III cell were 2.10 and 1.76 V. First discharge capacities of the DTA-III cathode and the GTA-III cathode were 113.3 and 134.7 Ah kg^{-1} , respectively; (these values were calculated from loaded weight of polyamide in the

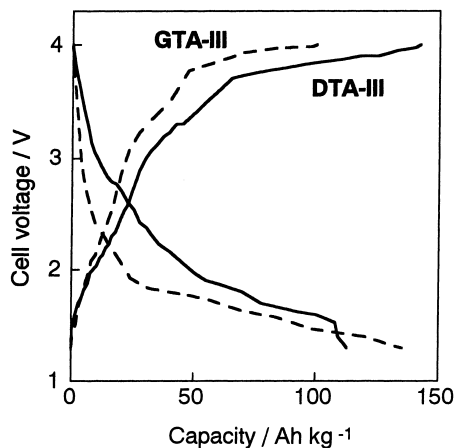


Fig. 7. Charge/discharge curves for Li/DTA-III and Li/GTA-III test cells. Electrolyte: PC-DME (1:1, by volume) containing $1 \text{ mol dm}^{-3} \text{ LiClO}_4$. Current density: 5 mA g^{-1} of polyamide. Cut off voltage: 1.3 and 4.0 V.

cathode). Energy density of the cathodes was estimated from Eq. (1).

$$\text{Energy density (estimated)} = \text{capacity of the cathode} \times \text{average discharge voltage} \quad (1)$$

Energy density in first discharge was 238 Wh kg^{-1} (DTA-III) and 237 Wh kg^{-1} (GTA-III). Estimated energy density of the Li/DTA-III cell in first discharge was almost equal to that of the Li/GTA-III cell. However, cycling performance was not similar with each other.

Fig. 8 shows variation of energy density (estimated from Eq. (1)) of the DTA-III- and the GTA-III- cathode with charge/discharge cycling. As mentioned above, the initial

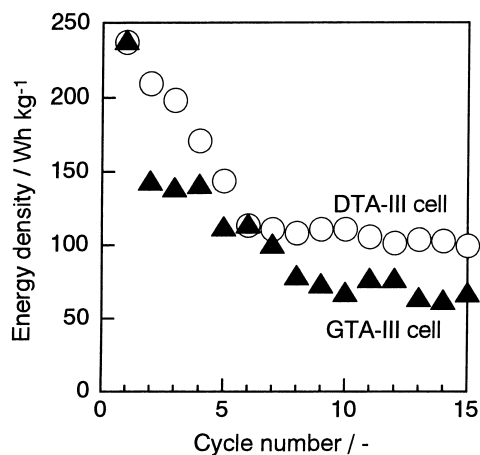


Fig. 8. Variation of energy density (estimated, see text) of DTA-III and GTA-III cathode with charge/discharge cycling. Condition was the same as that in Fig. 7.

energy density of the GTA-III cathode was almost equal to that of the DTA-III cathode. However, the value of the GTA-III cathode drastically decreased with increase in cycle number. At second cycle, energy density of the GTA-III cathode decreased to about half value of the first capacity. Continuous reduction of capacity for the GTA-III cathode was observed. In contrast, decrease in capacity of the DTA-III cathode was slow. Average discharge energy density (estimated from Eq. (1)) from the 1st to the 15th cycles of the DTA-III cathode was 135 Wh kg^{-1} and that of the GTA-III cathode was 100 Wh kg^{-1} . The cathode materials governed cycling performance of the test cells and the results agreed with those of the CV measurements for the polyamide electrodes. When the disulfide bonds in the polymer chain are cleaved under a discharge process, the GTA-III chains are divided, while the DTA-III chains are not. The cleavage of the polymer chain may be related with the loss of energy density of the Li/GTA-III cells.

However, the loss of energy density of the test cell with the DTA-III cathode was also observed with the charge/discharge cycles. Preparation method or configuration of cathode is one of the important points for a high performance cathode. Fan and Fedkiw reported the relation between cell performance and cathode (based on metal oxide, LiCoO_2 , LiMn_2O_4 , and LiNiO_2) preparation method, cast or high-pressure compacting [16]. They reported that the cell with the cast cathode that has high ohmic resistance could not be cycled and the cell with the high-pressure compacted cathode showed good cycling performance under high rate discharge. Our paste cathode showed decrease in capacity with repeated charge/discharge cyclings. This phenomenon may be closely related with conductivity of the mixture of polyamides and acetylene black powder. Further optimization of preparation of the polyamide cathode, such as preparation condition, mixing ratio, etc. should be done for construction of a high performance battery.

4. Conclusions

Polyamides with cyclic disulfide structure were prepared and electroactive in propylene carbonate- or ethylene carbonate-based electrolyte containing a lithium salt. Redox peaks were observed at 1.5 and 3.6 V versus Li/Li^+ . Polyamide with linear disulfide structure was also prepared and showed similar electrochemical behavior with the polyamides containing cyclic disulfide moiety. However, decrease of capacity of the linear polyamide electrode was more apparent than that of the polyamide with cyclic disulfide. Cleavage of linear-type polymer chain with redox cycling decreased the capacity of the electrode.

The test cells, Li/polyamide electrode cells, were constructed and their charge/discharge performance under constant current condition was investigated. Polymer structure also affected the utilization of the polyamide in the electrode and the cell cycling performance.

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