Preparation of Hyperbranch Polymer with Cyclic Disulfide and its Application to Positive Active Material of Secondary Battery

Hiromori Tsutsumi, Tomoyuki Nakagawa, Kenjiro Onimura, and Tsutomu Oishi Department of Applied Chemistry & Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1, Tokiwadai, Ube, Yamaguchi, 755-8611, Japan Fax: 81-836-85-9201, e-mail: tsutsumi@yamaguchi-u.ac.jp

Hyperbranch polyester with cyclic disulfide moiety was prepared from hyperbranch polyester and lipoic acid. The structure of the polymers was identified from the results of FTIR, NMR, and MALDI-TOF mass spectroscopy measurements. The electrodes with the hyperbranch polymers in the organic electrolyte solution (for example, the electrolyte solution containing propylene carbonate, 1, 2-dimethoxyethane, and LiBF₄) showed electrochemical responses based on the cyclic disulfide bonds. The redox potential and behavior of the disulfide bonds in the hyperbranch polymers were depended on its branch structure and generation. The capacity of the test cell with the positive electrode based on Lipo-D2 was 27.9 Ah kg⁻¹ and that based on Lipo-Tmp was 54.8 Ah kg⁻¹.

Key words: disulfide, hyperbranch polymer, positive active material, secondary battery

1. INTRODUCTION

A high-power secondary battery with thinner shape is one of the most important devices for lightening potable electrical equipment, such as portable telephone and portable computer. 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 storage secondary high-energy battery [1,2]. Electrochemical behavior and application of DMcT to cathode active material for lithium secondary batteries were investigated. Disadvantage point of DMcT is its solubility in typical organic solvent for lithium battery electrolytes, such as propylene carbonate (PC). Thus, solid or gel polymer electrolytes were used as an electrolyte for the cell with the DMcT cathode [3, 4].

We have been prepared various linear polyamides containing disulfide bonds in their main chains [-(-CO-R-S-S-R-CONH-R'-NH-)n-] containing disulfide bonds. Their electrochemical behavior and the performance of the test cells with the cathodes have been reported [5-9]. Furthermore, we reported the preparation of the polyamides containing cyclic disulfide structure and their application to positive active material for a lithium secondary battery [10].

Various hyperbranch polymers and dendrimers were prepared and their unique properties based on assembling functional groups on the molecular surface, multi-functional groups in one molecule, and their spherical shapes were investigated [11]. Assembling of functional groups on the molecular surface will increase reactivity of the functional groups.

We prepared new-type disulfide polymers that have a hyperbranch backbone and cyclic disulfide structures at the terminal of each branches (Fig. 1). Their electrochemical behavior in an organic electrolyte and possibility as positive active material were investigated.



Fig. 1 Structure of lipoic acid derivatives.

2. EXPERIMENTAL

The hyperbranch polymers were prepared from trimethylolpropane and 2,2-bis(hydroxymethyl)propionic acid following the literature [12]. Characterization of the polymers was performed with FTIR, NMR, and MALDI-TOF (Matrix Associated Laser Desorption/ Ionization Time of Flight) mass spectroscopy.

Detailed configuration of the carbon paste electrode for this study was described in our previous paper [5]. A mixture of polymer, acetylene black, and a small amount of polytetrafluoroethylene (PTFE) were blended with a mortar and pestle, and the paste was loaded on a copper mesh current collector. Typical loading levels of polymer on the electrode was 3 (polymer):7 (acetylene black) by weight. Cyclic voltammograms for the 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 of 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 the 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 a FTIR spectrometer (FTIR-4200, Shimadzu). Raman spectra of the compounds were also JASCO NR-1800 recorded with а Raman spectrophotometer. Solid state ¹³C CP/MAS (Cross Polarization and Magic Angle Spinning technique) NMR spectra of the polymers were measured with an NMR spectrometer with a magic angle spinning probe (CMX-300 Infinity, Chemagnetic). MALDI-TOF mass spectra of the polymers were recorded with a Voyager Biospectrometry Workstation. Sinapinic acid and a-cyano-4-hydroxycinnamic acid were used as a matrix reagent for the measurements [13].

3. RESULTS AND DISCUSSION

The structure of the hyperbranch polymers with cyclic disulfides were confirmed by the FTIR, NMR, and MALDI-TOF mass spectroscopy. Average degree of the induced lipoic acid moiety was 75.0% for Lipo-D1, 70.8% for Lipo-D2. Specific capacity of the polymers was corrected based on the values.

Electrochemical behavior of lipoic acid and the polymers was investigated with cyclic voltammetry technique. The voltammogram of lipoic acid/acetylene black (AB) paste electrode is shown in Fig. 2. Visco's group reported electrochemical properties of various organosulfur compounds in organic electrolyte solution [14-17]. However, electrochemical behavior of lipoic acid in an organic electrolyte has not been reported. We checked the electrochemical behavior of lipoic acid in an organic electrolyte solution.



Fig. 2 Cyclic voltammograms for lipoic acid/AB(30wt%) electrode in 1 mol dm⁻³ LiBF₄/PC-DME (1:1, by vol.)

Scan rate 10 mVs⁻¹

Cathodic peak at 3.6 V and anodic peak at 4.1 V were observed. Appearance of both peaks indicates that the cyclic disulfide bond in lipoic acid is electroactive in the organic electrolyte solution.

Fig. 3 shows the voltammograms for the Lipo-D1/AB paste electrode in PC-DME (1:1 by vol.) containing 1 mol dm⁻³ LiBF₄. Both cathodic and anodic peaks corresponded redox response of disulfide in the Lipo-D1 were observed at 3.8 V and 4.1 V, respectively. The electrochemical behavior of the Lipo-D1/AB electrode almost agrees with that of lipoic acid/AB paste electrode (see Figs. 2 and 3). The potential of cathodic peak shifted to positive and that of anodic one shifted to negative, slightly. This suggests that modification on the surface of the hyperbranch polymer affect the redox potential of disulfide in lipoic acid 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 [17].



Fig. 3 Cyclic voltammograms for Lipo-D1/AB(30wt%) electrode in 1 mol dm⁻³ LiBF₄/PC-DME (1:1, by vol.) Scan rate 10 mVs⁻¹

Electrochemical responses for Lipo-D2/AB electrodes were almost similar to that for the Lipo-D1/AB or lipoic acid/AB electrodes. Boarding of peaks in the voltamogram for Lipo-D2/AB electrode was observed. We recorded Raman spectra of the compounds with cyclic disulfide structure. Fig. 4 shows the Raman spectra of the compounds. The peak at *ca.* 525 cm⁻¹ is attributed to the stretching band of the S-S bond in the lipoic acid moiety. The spectrum for lipoic acid shows the sharp peak at 525 cm⁻¹. The corresponded peak for the other compounds, Lipo-Tme, Lipo-D1 and Lipo-D2, became broaden and splitting. This suggests that all of the disulfide bonds in the compound do not exist in the same condition. Therefore, their electrochemical reactivity is not same each other.

We constructed the test cells with the cathode including the hyperbranch polymers with cyclic disulfide structure. Charge-discharge cycling tests of the



Fig. 4 Raman spectra of lipoic acid and hyperbranched disulfide compounds.

cells were performed under constant current conditions. Fig. 5 shows typical charge and discharge curves of the test cell, Li/Lipo-Tme cell, current density at 8 mA cm⁻² (per surface area of cathode). The first discharge curve had flat region about 3.8 V. The first discharge capacity was 47.0 Ahkg^{-1} . Theoretical capacity of Lipo-Tme is 230.8 Ahkg⁻¹, calculated from two-electron transfer redox reaction of the disulfide bond on lipoic acid moiety. Utilization of loaded Lipo-Tme in the test cell was 20 %. The capacity of the test cell decreased with charge-discharge cycling condition. The results corresponded to the reducing peak current that of the cyclic voltammetry measurements of the electrode. Lipo-Tme is partially soluble in the electrolyte solution. Thus, the Lipo-Tme in the electrode dissolved into the electrolyte solution and the capacity of the cell decreased.



Fig. 5 Charge and discharge curves of Li|1 mol dm⁻³ LiBF₄/PC-DME |Lipo-Tme/AB(30wt%) test cell. Current density: 8 mA cm⁻² Cut off voltage: 3.0 and 4.3 V

Fig. 6 shows average and maximum capacities for the Lipo-Tme electrodes in PC-DME electrolytes containing a lithium salt used for lithium batteries, LiClO₄, LiBF₄, LiPF₆, and LiCF₃SO₃. Maximum capacity of the Lipo-Tme/AB electrode was 47.0 Ah kg⁻¹ in LiBF₄ electrolyte, 40.2 Ah kg⁻¹ in LiClO₄, 40.2 Ah kg⁻¹ in LiClO₄, 40.2 Ah kg⁻¹ in LiCF₃SO₃. Electrochemical stability of anion and/or conductivity of the electrolyte may be closely related with the salt dependence of capacity. Conductance between a current corrector and polymer and acetylene black particles affects the amount of reactive 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 LiPF₆ (8.8 mS cm⁻¹), LiClO₄ (5.7 mS cm⁻¹), LiBF₄ (3.3 mS cm⁻¹), and LiCF₃SO₃ (1.7 mS cm⁻¹) [18]. 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 LiBF₄ for electrolyte of test cells.



Fig. 6 Dependence of 1st and average capacity of test cell with Lipo -Tme / AB(30 wt%) electrode on lithium salt in PC-DME electrolyte.





Fig. 7 shows the capacity of the test cells with various hyperbranch polymers with cyclic disulfide structure and their model compounds. The capacity in Fig. 7 is compensated to the capacity per number of disulfide bond in the compounds. Theoretical maximum value is 193000 (96500 C mol⁻¹×2) C mol⁻¹. Utilization of the compounds in the test cell was estimated from the value. The utilization value was 20.4% for Lipo-Tme, 24.2% for Lipo-Tmp, 5.5% for Lipo-D1and 14.9% for Lipo-D2.

4. CONCLUSIONS

Hyperbranch polymers with disulfide bonds were prepared from hyperbranch polyester and lipoic acid. The structures were confirmed by FTIR, NMR, and MALDI-TOF mass spectroscopy. The degree of induced lipoic acid moiety in the polymer was 75.0% for Lipo-D1 and 70.8% for Lipo-D2.

All compounds prepared in this investigation were electroactive in the organic electrolyte solution, propylene carbonate/1,2-dimethoxyethane (1:1, by vol.) containing 1mol dm⁻³ LiBF₄. The electrochemical responses were depended on the structure of the hyperbranch polymer.

The test lithium secondary batteries with the lipoic acid derivatives, Lipo-Tme, -Tmp, -D1, and -D2, were constructed and the charge-discharge performance of the cells was recorded under the constant current condition. The cell performance depended on the current density of the cycling test, lithium salt for the electrolyte solution, and the kind of the lipoic acid derivatives.

Utilization of the disulfide bonds in the positive electrode was 20.4% for Lipo-Tme, 24.2% for Lipo-Tmp, 5.5% for Lipo-D1, and 14.9% for Lipo-D2, respectively.

ACKNOWLEDGEMENTS

This work was performed using facilities of the Yamaguchi Prefectural Industrial Technology Institute (MALDI-TOF mass spectrometer) and the Collaborative Research Center Yamaguchi University (solid state NMR spectrometer). REFERENCES

[1] M. M. Doeff, S. J. Visco, and L. C. D. Jonghe, J. Applied Electrochemistry, **22**, 307-309 (1992).

[2] N. Oyama, T. Tatsuma, T. Sato, and T. Sotomura, *Nature*, **373**, 598-600 (1995).

[3] T. Sotomura, H. Uemachi, K. Takeyama, K. Naoi, and N. Oyama, *Electrochimica Acta*, **37**, 1851-1854 (1992).

[4] M. M. Doeff, S. J. Visco, and L. C. D. Jonghe, J. *Electrochem. Soc.*, **139**, 1808-1812 (1992).

[5] H. Tsutsumi and K. Fujita, *Electrochimica Acta*, 40, 879-882 (1995).

[6] H. Tsutsumi, K. Okada, and T. Oishi, *Electrochimica* Acta, **41**, 2657-2659 (1996).

[7] H. Tsutsumi, K. Okada, K. Fujita, and T. Oishi, J. Power Sources, **68**, 735-738 (1997).

[8] H. Tsutsumi, S. Okada, and T. Oishi, *Electrochimica Acta*, **43**, 427-429 (1998).

[9] H. Tsutsumi, S. Okada, K. Toda, K. Onimura, and T. Oishi, *Mat. Res. Soc. Symp. Proc.*, **496**, 323-328 (1998).

[10] H. Tsutsumi, Y. Oyari, K. Onimura, and T. Oishi, J.
Power Sources, 92, 228-233 (2001).

[11] G. R. Newkome, C. N. Moorefield, and F. Vogtle, "Dendrimers and Dendrons; Concepts, Synthesis, Perspectives", Wiley-VCH, Weinheim, (2001).

[12] E. Malmstrom, M. Johansson, and A. Hult, Macromoleclues, 28, 1698 (1995).

[13] M. W. F. Nielen, Mass Spectrometry Reviews, 18, 309-344 (1999).

[14] M. Liu, S. J. Visco, and L. C. D. Jonghe, J. Electrochem. Soc., **136**, 2570-2575 (1989).

[15] M. Liu, S. J. Visco, and L. C. D. Jonghe, J. *Electrochem. Soc.*, **137**, 750-759 (1990).

[16] M. Liu, S. J. Visco, and L. C. D. Jonghe, in The Electrochemical Society, Vol. PV 91-3 (K. M. Abraham and M. Solomon, eds.), The Electrochemical Society, (1991) p. 62-74.

[17] M. Liu, S. J. Visco, and L. C. D. Jonghe, J. *Electrochem. Soc.*, **138**, 1896-1901 (1991).

[18] M. Ue, *Prog. Batteries and Battery Materials*, **14**, 137 (1995).

(Received December 21, 2002; Accepted January 25, 2003)