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Electrochemically active copolymers prepared from elemental sulfur and bis(alkenyl)
compounds having crown ether unit

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Abstract

We prepared random copolymers from elemental sulfur (S) and bis(alkenyl) compound with crown ether (BUMB18C6). The resulted random copolymers, poly(S-*r*-BUMB18C6) were soluble in the organic solvents, tetrahydrofuran, *N*-methyl-2-pyrrolidone, and chloroform. The Ketjenblack (KB) and acetylene black (AB) particles were treated with the copolymer solution. TEM and EDS results of the treated carbon particles indicate that the incorporation of the copolymer into the KB cavities. The attachment of the copolymer to the AB particles was not observed, obviously. The copolymers in the KB particles showed the electrochemical responses based on the redox reaction of their polysulfide chains in organic electrolyte solution (1.0 mol dm^{-3} lithium bis(trifluoromethane)sulfonamide in 1:1 (v/v) mixture of 1,3-dioxolane and 1,2-dimethoxy-ethane). The lithium coin cells having the copolymer electrode were constructed and their charge-discharge behaviors were also tested under constant current conditions. Coulombic efficiency the test cells with poly(S-*r*-BUMB18C6-0.5)/KB electrode was over 95 % at 100th cycle and the average capacity through the 100 cycles was 286 Ah kg^{-1} .

1. Introduction

Preparations of many polymers containing mono-, di-, tri-, or polysulfide bonds and their applications have been investigated by many scientists and engineers [1]. For example, poly(disulfide)s having disulfide bonds in their main or side chains showed many functions, such as self-sorting, building supramolecular systems [2].

Poly(disulfide)s have been also investigated as positive active materials for lithium secondary batteries. Electrochemical cleavage and reforming of disulfide bonds was used as high capacity positive active materials [3-19]. Slow reaction rate of cleavage and reforming of disulfide bonds prevented practical application of poly(disulfide)s to positive active materials.

Recently, lithium (Li)-sulfur (S) batteries are one of the most cost-effective energy storage systems. Elemental sulfur is electrical and ionic insulator, low reactive material near room temperature, and forms its soluble species that are lithium polysulfides (Li_2S_n , $n > 4$) at the discharge process in the Li-S batteries. The properties of sulfur provide the low utilization and poor cycle characteristics of Li-S batteries. Many scientists and

engineers have improved the disadvantage points of sulfur positive electrodes [20-23]. The typical approach is preparation of the enclosed sulfur particles with conductive materials, various carbon materials or conductive polymers. The enclosed small sulfur particles or micrometer-sized sulfur wires with carbon materials [20, 21, 24] or conductive polymers [25-29] have been reported. Polymer compounds which have redox active sulfide structure such as disulfide have been prepared and their electrochemical properties and application to battery systems have been also investigated [3-19]. A few polymer compounds with oligo-sulfide chains ($-S_n-$, $n > 2$) have been prepared. Chung, *et al.*, have reported the reaction between organic compounds with double bonds and elemental sulfur, called ‘inverse vulcanization’ and application of the resulted random copolymers to various fields, positive active material for lithium secondary batteries [30].

Our approach is using copolymer from elemental sulfur and bis(alkenyl) compound having crown ether (Fig. 1) as a positive active material.

Fig. 1 Structures of bis(alkenyl) compound having crown ether (BUMB18C6).

In this paper we report about the preparation of the random copolymers from sulfur and bis(alkenyl) compound having crown ether unit and their electrochemical behavior in an organic electrolyte solution. The bis(alkenyl) compound has crown ether moiety or linear ether unit as shown in Fig. 1, bis(undec-10-enoyloxymethylbenzo)-18-crown-6 ether, BUMB18C6. Electrochemical behavior of the copolymer in the organic electrolyte solution was also reported. Lithium-copolymer test cells were also constructed and their performances were checked under constant current charge-discharge conditions.

2. Experimental

All reagents were purchased and used without further purification unless otherwise stated. Scheme 1 shows preparation route of BUMB18C6.

Bis(formylbenzo)-18-crown-6 ether (**1**) and bis(hydroxymethylbenzo)-18-crown-6 ether, (**2**) were prepared by the similar procedure of the literature [31, 32]. NMR and MS spectra of BUMB18C6 were shown in Fig. S1, S2, and S3 (*see* Supplementary information).

Scheme 1 Preparation route of BUMB18C6.

2.1 Preparation of bis(undec-10-enoyloxymethylbenzo)-18-crown-6 ether (BUMB18C6)

Bis(10-undecenoyloxymethylbenzo)-18-crown-6 ether were prepared by coupling reaction between bis(hydroxymethylbenzo)-18-crown-6 ether and 10-undecenoyl chloride. Bis(hydroxymethylbenzo)-18-crown-6 ether (Molecular weight is 420.45, 1.9 g, 4.52 mmol,) was dissolved in dichloromethane, and triethylamine (5.61 g, 55.4 mmol) was added to the solution. To the solution was added dropwise a solution of 10-undecenoyl chloride (11.2 g, 55.4 mmol) in dichloromethane. The mixture was stirred at room temperature for 24 h. After the stirring, a saturated aqueous solution of NaHCO_3 was poured in the reaction mixture, followed by extraction with dichloromethane. The organic layer was dried over magnesium sulfate and evaporated under reduced pressure to give a residue as yellow oil. The residue was purified by

column chromatography (SiO₂, *n*-hexane/ EtOAc (1:1)), followed by washing with diethylether/*n*-hexane to give bis(undec-10-enoyloxymethylbenzo)-18-crown-6 ether (BUMB18C6) as a white solid (0.71 g, 21 %).

¹H NMR (500 MHz, CDCl₃; δ, ppm): δ 6.92-6.79(m, 6H, Ph), 5.89-5.73(m, 2H, CH₂=CH-), 5.05-4.88(m, 8H, CH₂=CH-, Ph-CH₂-O-CO-), 4.15-4.13(m, 8H, -CH₂-CH₂-O-), 3.92-3.83(m, 8H, -CH₂-CH₂-O-), 2.36-2.26(m, 4H, -CH₂-COO-), 2.08-1.96(m, 4H, CH₂=CH-CH₂-), 1.70-1.55(m, 4H, -CH₂CH₂-COO-), 1.43-1.20(m, 20H, CH₂=CH-CH₂-(CH₂)₅-).

¹³C NMR (125 MHz, CDCl₃; δ, ppm): δ 173.7 (C=O), 148.7 (Ph), 139.1 (CH₂=CH-), 129.0 (Ph), 121.5 (Ph), 114.1 (CH₂=CH-), 113.9 (Ph), 113.2 (Ph), 69.8 (-Ph-CH₂CH₂O-), 68.8 (-Ph-CH₂CH₂O-), 66.0 (-COO-CH₂-Ph-), 34.3 (Alkyl), 33.7 (Alkyl), 29.0 (Alkyl), 24.9 (Alkyl).

Elemental analysis: obs. 69.986 % C, 8.608 % H, calc. for C₄₄H₆₄O₁₀ 70.18 %C, 8.57 % H.

HR-ESI-MS: m/z 775.4411 [M+Na]⁺ (calc. C₄₄H₆₄O₁₀, 752.499)

Sodium ions in the MS sample due to the eluent solution for an ultra-performance

liquid-chromatography tandem mass spectrometry (UPLC-MS) system were observed.

2.2. Copolymerization between elemental sulfur and bis(alkenyl) compounds

(BUMB18C6) Typical preparation procedure of poly(S-*r*-bis(alkenyl)compound-*a*) is as follows: To test tube equipped with magnetic stir bar was added sulfur (S₈ 0.40 g, 1.6 mmol) and bis(alkenyl) compound (BUMB18C6, 0.376 g, 0.5 mmol), the tube was then heated to 428 K in a temperature-controlled oil bath for 10 minutes. The resulting mixture was stirred at 433 K until stirring stopped, and the mixture kept at 433 K for 1 hour. Furthermore, the mixture left in the oil bath at 443 K for 1.5 h. The product was then taken directly from the test tube using a spatula after allowing the reaction mixture to cool to room temperature. The product is referred as poly(S-*r*-BUMB18C6-0.5). The resulted weight of poly(S-*r*-BUMB18C6-0.5) was 0.776 g (Yield was *ca.* 100%). We also prepared the poly(S-*r*-BUMB18C6-0.1) from the mixture sulfur (S₈ 0.40 g, 1.6 mmol) and BUMB18C6 (0.075 g, 0.1 mmol). The yield was also *ca.* 100% (0.475 g).

¹H NMR of poly(S-*r*-BUMB18C6-0.5) (500 MHz, CDCl₃; δ, ppm): δ 6.92-6.79(m, 6H, Ph), 5.05 (s, 4H, Ph-CH₂-O-CO-), 4.15-4.13 (m, 8H, -CH₂-CH₂-O-Ph), 3.92-3.83 (m, 8H, -CH₂-CH₂-O-Ph), 3.20-3.05 (m, 2H, -S-CH₂-CH(-S)-CH₂-), 3.05-2.82 (m, 4H,

-S-CH₂-CH(-S-)-CH₂-), 2.50-2.25 (m, 4H, -CH₂-COO-), 1.80-1.55 (m, 4H, -CH₂CH₂-COO-), 1.50-1.10 (m, 20H, -S-CH₂-C(S-)H-CH₂-(CH₂)₅-)

Similar spectra were observed in poly(S-*r*-BUMB18C6-0.1). Fig. S4(a) and (b) shows ¹H NMR spectra of poly(S-*r*-BUMB18C6-*a*, *a* = 0.1 or 0.5).

*2.3 Preparation of poly(S-*r*-BUMB18C6-*a*) electrode sheet for electrochemical measurements*

Typical preparation procedure of poly(S-*r*-BUMB18C6-*a*, *a* = 0.1 or 0.5) electrode sheet is as follow: Poly(S-*r*-BUMB18C6-*a*) was combined with conductive carbon, Ketjenblack (KB, EC-600 JD, Lion, its specific surface area is 1270 m²g⁻¹) or acetylene black (AB, Denka, its specific surface area is 65 m²g⁻¹), and polytetrafluoroethylene (PTFE) as a binder in mass ratio of 60:30:10, respectively, and mixed into a slurry solution with chloroform. The slurry was heated at 333 K for 30 minutes to remove the chloroform, and pressed at 443 K. The resulted sheets were used as an electrode for electrochemical measurements and charge-discharge test cell construction. The resulted sheets with poly(S-*r*-BUMB18C6-0.1) compound were brittle and difficult to handle in the further investigations. We mainly used the electrode with poly(S-*r*-BUMB18C6-0.5) compound in this investigation.

2.4 Measurements

^1H NMR spectra of the resulted copolymer were recorded with an NMR spectrometer (JNM-Lamda500, JEOL). Mass spectra of crown ether derivatives were obtained with TOF-MS (LCT Premier XE, Waters). MALDI-TOFMS (matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy) spectra of the resulted copolymer (poly(S-*r*-BUMB18C6-0.5)) were measured with a MALD-TOFMS spectrometer (AXIMA-Performance, Shimadzu/KRATOS). A mixture (1:1 by vol.) of dithranol (20 mg ml⁻¹ in THF) and sodium trifluoroacetate (10 mg ml⁻¹ in THF) was used as a matrix reagent. Angiotensin II and ACTH19-38 were used as external standards for the measurements.

Molecular weight of the copolymers was measured with a GPC (gel permeation chromatography) technique. The measurements were performed with a Shimadzu Prominence system, LC-20AD (pump), SPD-20A (UV detector), CTO-20A (column oven), and column Shodex GPC KF-804 L (Showa Denko, column size 8.0φ×300 mm×2 (in series)). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 ml min⁻¹. From the GPC results, the molecular weight was determined as calibrated with polystyrene standards.

The morphology of the Ketjenblack particles modified with poly(S-*r*-BUMB18C6-0.5) was analyzed by transmission electron microscopy (TEM; JEOL JEM-2100) fitted with a CCD camera at an acceleration voltage of 200 kV. The samples were prepared by spreading a small drop of ultrasonic dispersed the polymer-modified Ketjenblack or acetylene black particles into ethanol on carbon-coated copper grid, allowed to dry in air at room temperature for about 12 h. The energy dispersive spectroscopy (EDS) elemental mapping experiments were performed from the TEM micrograph in the same instrument.

Electrochemical measurements were performed with a three-electrode conventional cell. The electrolyte used was 1.0 mol dm⁻³ lithium bis(trifluoromethane)sulfonamide (LiTfSA) in 1:1 (v/v) mixture of 1, 3-dioxolane (DOX) and 1, 2-dimethoxy ethane (DME). The circle-cut sheet (6 mm) on a glassy carbon current collector was used as the working electrode. The reference electrode was a Li foil (5 mm by 3 mm) and the counter electrode was a Li foil (20 mm by 20 mm). All of the electrochemical measurements were performed with a computer-controlled potentiogalvanostat (HZ-5000, Hokuto Denko) under Ar atmosphere (dew point was under 203 K) at 301 K. The current density was normalized by the weight of sulfur in the electrode. A coin type test cell (size 2032) was constructed with positive electrode, a lithium foil, the

electrolyte (1 mol dm⁻³ LiTFSa, DOX-DME, 1:1, by vol.) and a separator (CelgardTM 2500). Charge-discharge cycle performance of the test cells was checked with a charge-discharge cyler (HJ1001SD8, Hokuto Denko). Typical charge-discharge cycle test condition under constant current was at charge-discharge rate of 0.1 C (1C = 1675 A kg⁻¹ sulfur) and cutoff voltage range between 1.5 V and 2.7 V.

3. Results and Discussion

*3.1 Structures of poly(S-*r*-BUMB18C6-*a*) and mixture between carbon materials and poly(S-*r*-BUMB18C6-*a*)*

Insoluble property of sulfur into common organic solvents is inconvenience for mixing sulfur with a conductive additive, for example, acetylene black or Ketjenblack. The resulted copolymer, poly(S-*r*-BUMB18C6-*a*), *a* = 0.1 and 0.5, is elastic and soluble into the conventional organic solvents, tetrahydrofuran, *N*-methyl-2-pyrrolidone, and chloroform. Disappearance of the double bonds (attributed to the bis(alkenyl) group) by addition of sulfur was confirmed with ¹H-NMR spectra of poly(S-*r*-BUMB18C6-*a*), *a* = 0.1 and 0.5 (see Fig. S4 (a) and (b)). The results suggest that elemental sulfur is copolymerized with BUMB18C6. The estimated structure of poly(S-*r*-BUMB18C6-0.5) is shown in Fig. 2.

Fig. 2 Estimated structure of poly(S-*r*-BUMB18C6-0.5)

The average molecular weight of poly(S-*r*-BUMB18C6-*a*), *a* = 0.1 and 0.5 was about 1400 - 2400 determined by GPC measurements. MALDI-TOFMS spectra (*see* Supplementary information, Fig. S5 and Table S1) of poly(S-*r*-BUMB18C6-*a*), *a* = 0.1 or 0.5 suggest that the attached number of sulfur atoms to one BUMB18C6 molecule (*M* = 752.45) is from 4 (*m/z* = 903.4, [*M*+Na⁺+S₄]) to 11 (*m/z* = 1127.2, [*M*+Na⁺+S₁₁]). It suggests that longer sulfide chains (over 12 sulfur atoms' attachment per one BUMB18C6 molecule) are small amount in the copolymer which is prepared from elemental sulfur and the bis(alkenyl) compound with cyclic ether.

Fig. 3 and 4 shows the TEM images of the Ketjenblack (KB) particles and the acetylene black (AB) particles modified with poly(S-*r*-BUMB18C6-0.5) and EDS

mapping results.

Fig. 3 TEM of (a) Ketjenblack powders modified with poly(S-*r*-BUMB18C6-0.5) copolymer and corresponding quantitative EDS element mapping of (b) C, (c) O and

Fig. 4 TEM of (a) acetylene black powders modified with poly(S-*r*-BUMB18C6-0.5) copolymer and corresponding quantitative EDS element mapping of (b) C, (c) O and

The EDS mapping images of carbon (C), oxygen (O), and sulfur (S) are also presented.

The EDS mapping image of S indicates the presence of sulfur with the KB particles (Fig.

3 (d)). On the AB particles the amount of sulfur atoms is very few from the mapping

image of S on the AB particles, as shown in Fig. 4 (d). The KB particles had a hollow

structure (core) and many mesopores [33]. The comparison of TEM image between Fig

3 and Fig. 4 indicates that the poly(S-*r*-BUMB18C6-0.5) was incorporated into the core

of the KB particles and not into the AB.

*3.2 Electrochemical responses of poly(S-*r*-BUMB18C6-0.5)/KB or AB electrode*

Fig. 5 (a) shows the cyclic voltammograms of the poly(S-*r*-BUMB18C6-0.5)/KB electrode in the organic electrolyte solution, 1 mol dm⁻³ LiTFSA, DOX-DME (1:1, by vol.). Current density was normalized by the weight of sulfur in the electrode.

At first cathodic scan the electrode shows increase in cathodic current corresponding to the reduction of the copolymer. The cathodic overlapped peaks at around 2.3 – 2.4 V are related to the production of the higher-order lithium polysulfides (Li₂S_n, $n > 4$) [23]. The broader and large cathodic peak at around 1.85 V is attributed to the production of the lithium sulfide (Li₂S) [23]. The anodic peak at 2.52 V with slight shift under continuous cycling suggests that electrochemical stability of the oxidation reactions. At 8th cycling, the shape of voltammogram became simple and two redox peaks at 2.0 V and 2.5 V were observed. This suggests that the chemical species in the copolymer electrode are simplified under the potential cycling, due to the dissolution of long polysulfide into the electrolyte.

Fig. 5 (b) shows the voltammograms at 8th cycle of poly(S-*r*-BUMB18C6-0.5)/KB electrode and poly(S-*r*-BUMB18C6-0.5)/AB electrode in the organic electrolyte. The

peak current of the poly(S-*r*-BUMB18C6-0.5)/KB electrode was about ten times higher than that of poly(S-*r*-BUMB18C6-0.5)/AB electrode. This indicates that the amount of copolymer in the core of KB particle is larger than that on the AB particles. This observation agrees to the TEM results as mentioned before section.

Fig. 5 Cyclic voltammograms of the poly(S-*r*-BUMB18C6-0.5)/KB electrode (a) and voltammograms at 8th cycle of the poly(S-*r*-BUMB18C6-0.5)/KB electrode and poly(S-*r*-BUMB18C6-0.5)/AB electrode (b) in the organic electrolyte solution (1.0 mol dm⁻³ lithium bis(trifluoromethane)sulfonamide in 1:1 (v/v) mixture of 1,3-dioxolane and 1,2-dimethoxy ethane). Scan rate at 0.5 mVs⁻¹.

3.3 Charge-discharge performance of the test coin cells

Fig. 6 shows the charge-discharge curves of the test coin cell, Li|poly(S-*r*-BUMB18C6-0.5)/KB cell, under constant current condition (0.1 C, 1 C = 1675 Akg⁻¹). The voltage plateaus in the discharge curves were observed around 2.0 V.

(The voltage values are close to the peak positions on the cyclic voltammogram of the poly(S-*r*-BUMB18C6-0.5)/KB electrode as shown in Fig. 5.) The capacity is converted into the value per the sulfur weight in the copolymer. The capacity of the test cell was 606 Ah kg⁻¹ at 1st discharge cycle and 228 Ah kg⁻¹ at 100th discharge cycle. The average capacity through the 100 cycles was 286 Ah kg⁻¹. The average columbic efficiency was over 95 % (Fig. 7). The cycle durability of the test cell and high columbic efficiency are due to (1) effective trap of the copolymer by the Ketjenblack microporous cores [34] and (2) produced shorter sulfide structure in the copolymer to prevent formation of polysulfide anion with long sulfur chain [35]. Crown ethers are well known as a cation trapping host [36]. Coexistence of crown ethers in the electrolyte solutions have affected the conductance of the electrolyte solutions [37]. Crown ether moiety in the poly(S-*r*-BUMB18C6) will also affects performance of the Li secondary test cells. The studies about the effect of crown ether moiety in the copolymers on the electrode performance are now in progress.

Fig. 6 Charge-discharge curves with cycle number of Li|poly(S-*r*-BUMB18C6-0.5) test coin cell (2032 type). Charge-discharge rate at 0.1C (1C = 1675 A kg⁻¹) and cutoff voltage range between 1.5 V and 2.7 V.

Fig. 7 Variation of discharge capacity and the columbic efficiency with cycle number (*n*) of Li|poly(S-*r*-BUMB18C6-0.5) test coin cell (2032 type). Charge-discharge rate at 0.1C (1C = 1675 A kg⁻¹) and cutoff voltage range between 1.5 V and 2.7 V.

4. Conclusion

We prepared soluble and elastic copolymer, poly(S-*r*-BUMB18C6-*a*) (*a* = 0.1 or 0.5), from elemental sulfur and bis(alkenyl)compound with crown ether.

Poly(S-*r*-BUMB18C6-0.5) was electrochemically active and showed responses based on polysulfide in it. The test cell, Li|poly(S-*r*-BUMB18C6-0.5) cell provided good performance under constant current charge-discharge conditions, 606 Ah kg⁻¹ at 1st cycle, and 286 Ah kg⁻¹ (average capacity through 100 cycles).

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Figure captions

Fig. 1 Structure of bis(alkenyl) compound with crown ether moiety (BUMB18C6) .

Fig. 2 Estimated structure of poly(S-*r*-BUMB18C6-0.5) copolymer.

Fig. 3 TEM of (a) Ketjenblack powders modified with poly(S-*r*-BUMB18C6-0.5) copolymer and corresponding quantitative EDS element mapping of (b) C, (c) O and (d) S.

Fig. 4 TEM of (a) acetylene black powders modified with poly(S-*r*-BUMB18C6-0.5) copolymer and corresponding quantitative EDS element mapping of (b) C, (c) O and (d) S.

Fig. 5 Cyclic voltammograms of the poly(S-*r*-BUMB18C6-0.5)/KB electrode (a) and voltammograms at 8th cycle of the poly(S-*r*-BUMB18C6-0.5)/KB electrode and poly(S-*r*-BUMB18C6-0.5)/AB electrode (b) in the organic electrolyte solution (1.0 mol dm⁻³ lithium bis(trifluoromethane)sulfonamide in 1:1 (v/v) mixture of 1,3-dioxolane and 1,2-dimethoxy ethane). Scan rate at 0.5 mVs⁻¹.

Fig. 6 Charge-discharge curves with cycle number of Li|poly(S-*r*-BUMB18C6-0.5)/KB test coin cell (2032 type). Charge-discharge rate at 0.1C ($1C = 1675 \text{ A kg}^{-1}$) and cutoff voltage range between 1.5 V and 2.7 V.

Fig. 7 Variation of discharge capacity and the columbic efficiency with cycle number (n) of Li|poly(S-*r*-BUMB18C6-0.5)/KB test coin cell (2032 type). Charge-discharge rate at 0.1C ($1C = 1675 \text{ A kg}^{-1}$) and cutoff voltage range between 1.5 V and 2.7 V.

THF

Electrochemically active