



Soluble sulfur-based copolymers prepared from elemental sulfur and alkenyl alcohol as positive active material for lithium-sulfur batteries



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ABSTRACT

We prepared random copolymers from elemental sulfur (S) and alkenyl alcohol (10-undecen-1-ol, UDOL). The copolymers, poly(S-*r*-UDOL), have hydroxyl groups in their side chain and are soluble into the organic solvents, tetrahydrofuran (THF), *N*-methyl-2-pyrrolidone and chloroform. The Ketjen Black (KB) powder which included poly(S-*r*-UDOL) in its pores, poly(S-*r*-UDOL)@KB, was prepared by dipping KB powder into the THF solution with poly(S-*r*-UDOL). The poly(S-*r*-UDOL)@KB electrode showed the electrochemical responses based on the redox reaction of polysulfide chains in poly(S-*r*-UDOL). The assembled cells with the poly(S-*r*-UDOL)@KB as a positive active material and lithium as a negative active material showed high discharge capacity at 1st cycle and low cycle performance under constant current charge-discharge conditions. Treatment of the poly(S-*r*-UDOL)@KB with hexamethylene diisocyanate (HDI) was effective in retention of the cell capacity. Formation of crosslinked structure between poly(S-*r*-UDOL) molecules in the KB pores through urethane bonds improved capacity retention of the Li- poly(S-*r*-UDOL) electrode battery system.

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1. Introduction

Elemental sulfur (S) is one of the most attractive candidates as high capacity (1675 Ah kg⁻¹) and low cost positive active material for lithium (Li) secondary batteries. However, sulfur is electrical and ionic insulator, low reactive material around room temperature, and its reduced species, lithium polysulfides (Li₂S_{*n*}, *n* > 4) is soluble into an organic electrolyte solution with Li ions. The properties of elemental sulfur provide low utilization and poor cycle performance of Li-S batteries. Many scientists and engineers have improved the disadvantage points of sulfur positive electrodes [1–4].

Typical approach for improvement is preparation of the wrapped sulfur particles with conductive materials, conductive polymers or various carbon materials. The wrapped small sulfur particles or micrometer-sized sulfur wires with conductive polymers [5–9] or carbon materials [1,2,10] have been reported.

Another approach is using small size sulfur allotropes (S_{*n*}, *n* = 2, 3, and 4) confined in a microporous carbon matrix as a positive material [11]. The small size sulfur allotropes do not produce unfavorable soluble chemical species (Li₂S_{*n*}, *n* = 4–8) in their reduction process (discharge process in the Li-S battery systems).

Reaction between organic compounds with double bonds and sulfur is typically used as vulcanization process of natural rubber [12]. Chung, et al., have reported the reaction between organic compounds with double bonds and elemental sulfur, called ‘inverse vulcanization’ [13]. Applications of the resulted random copolymers to various fields such as positive active material for lithium secondary batteries and materials for defense or for sustainability have been reported [14–18]. The copolymerization process starts with ring opening of elemental sulfur (8-membered ring structure) and formation of linear biradicals (*-S₈-*); * means radical species) by heating over its melting point. Copolymerization between sulfur and alkenyl compound provide us with soluble compounds having polysulfide chains [19,20]. However, the reported copolymers had no reactive functional groups for post-processes such as crosslink or other chemical modifications.

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Our approach in this report is using copolymers, poly(S-*r*-UDOL), prepared from elemental sulfur (S) and simple alkenyl alcohol (10-undecen-1-ol, UDOL, Scheme 1) as a positive active material. The sulfur-containing copolymers have functional group, hydroxyl group for post-process and chemical modification. Support of the electroactive polymers on porous carbon materials, such as Ketjenblack, KB [21,22] will provide us with high performance and durability of sulfur-based electrodes for Li secondary batteries. We tested the assembled cells with the copolymer as a positive active material and a Li electrode as a negative active material. Effect of crosslink reagent, hexamethylene diisocyanate (HDI), which has reactive isocyanate groups with hydroxyl groups, on charge-discharge cycle characteristic of poly (S-*r*-UDOL) based positive electrode, was also investigated.

2. Materials and methods

All reagents were purchased and used without further purification unless otherwise stated.

2.1. 2.1 Copolymerization between elemental sulfur and 10-undecen-1-ol

Typical preparation procedure (Scheme 1) of poly(S-*r*-UDOL-1.0) is as follows: To a test tube equipped with a magnetic stir bar was added sulfur (0.256 g, 8.0 mmol) and heated at 448 K. After the sulfur melted, 10-undecen-1-ol (0.170 g, 1.0 mmol) was slowly added to the test tube at 448 K. The mixture was stirred for 3 h at 448 K. 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*-UDOL-1.0). The yield of poly(S-*r*-UDOL-1.0) was ca. 100%. We also prepared the poly(S-*r*-UDOL-*x*), *x* = 0.1, 0.5, and 2.0, copolymer from the mixture of sulfur (8 mmol) and UDOL (*x* mmol) with quantitative yield.

¹H NMR (CDCl₃) of poly(S-*r*-UDOL-1.0) (δ , ppm from TMS): 3.62(2H, t, *J* = 6.25, CH₂OH), 2.5–3.5(2H, m, S-CH₂), 1.73(2H, s, CH₂-CH-S), 1.5–1.75(1H, m, S-CH), 1.55(2H, m, CH₂CH₂OH), 1.39–1.29(12H, br, (CH₂)₆).

IR (cm⁻¹) 3300 (–OH, stretching of O-H), 2750–3000 (–CH₂–, stretching of C-H), disappearance peak 1650 (C=C, stretching of C=C).

Similar spectra were observed in poly(S-*r*-UDOL-*x*), *x* = 0.1, 0.5 and 2.0, composites (Fig. A2). Elemental analysis results of poly(S-*r*-UDOL-*x*), *x* = 0.1, 0.5, 1.0, and 2.0 are listed in Table A2 in Appendix A.

2.2. 2.2 Preparation of poly(S-*r*-UDOL-*x*)@KB composites

Typical procedure for preparation of poly(S-*r*-UDOL-*x*)@KB composites is as follows: Poly(S-*r*-UDOL-1.0) (0.5008 g) was

dissolved into tetrahydrofuran (THF, 5 mL) at room temperature. Ketjen Black (KB, EC600JD, Lion) (0.2554 g) was added into the THF solution and the THF solution was stirred for 1 h at room temperature. Then the THF was removed by dynamic vacuum condition (333 K) for 24 h. The resulted composite is referred as poly(S-*r*-UDOL-1.0)@KB composite. Other copolymer-KB composites, poly(S-*r*-UDOL-*x*)@KB, *x* = 0.1, 0.5, and 2.0, were also prepared with similar procedure.

2.3. 2.3 Preparation of poly(S-*r*-UDOL-*x*)@KB electrode sheet for electrochemical measurements

Preparation procedure of poly(S-*r*-UDOL-1.0)@KB electrode sheet is as below: poly(S-*r*-UDOL-1.0)@KB powder (0.45 g, the composition was 0.30 g of poly(S-*r*-UDOL-1.0) and 0.15 g of KB) was added into the sodium alginate (Na-Alg) viscous aqueous solution (5 mL) (0.0521 g of Na-Alg was contained). The resulted slurry was coated onto an aluminum foil and heated for 24 h at 353 K to remove the water. Other composite electrodes, poly(S-*r*-UDOL-*x*)@KB electrodes, *x* = 0.1, 0.5, and 2.0 were also prepared with similar procedure.

2.4. 2.4 Preparation of cross-linked poly(S-*r*-UDOL-1.0)@KB composite and its electrode

Cross-linking of poly(S-*r*-UDOL-1.0) which was incorporated in the KB pores was performed by using hexamethylene diisocyanate (HDI). Poly(S-*r*-UDOL-1.0)@KB composite (0.9420 g, poly(S-*r*-UDOL-1.0) 0.6105 g and KB 0.3315 g) was dispersed into *n*-hexane (10 mL) at room temperature. HDI (0.1203 g, 0.7152 mmol) was dropwise added into the dispersion and then stirred at room temperature (293 K–298 K) for 5 h under Ar atmosphere. To remove the *n*-hexane, the resulted dispersion was heated at 353 K for 24 h. The resulted compound is referred as poly(S-*r*-UDOL-1.0)-HDI@KB. The poly(S-*r*-UDOL-1.0)-HDI@KB electrode sheets for electrochemical measurements were also prepared by similar procedure as mentioned before.

2.5. 2.5 Measurements

¹H spectra of the resulted copolymers were recorded with an NMR spectrometer (JNM-Lamda500, JEOL). Molecular weight of the copolymers was measured with a GPC (gel permeation chromatography) technique (apparatus and detail conditions were shown in Table A2).

Electrochemical measurements and charge-discharge tests were performed with a coin type test cell (size 2032) having a circle-cut poly(S-*r*-UDOL-*x*)@KB or poly(S-*r*-UDOL-1.0)–HDI@KB sheet (10 mm ϕ), a Li foil (10 mm ϕ) as a reference and counter electrode and a circle-cut glass filter paper (Advantec, 10 mm ϕ).



Scheme 1. Preparation route of poly(S-*r*-UDOL) from sulfur (S) and 10-undecen-1-ol (UDOL), *n* and *m* > 0–8.

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