



X-ray absorption near edge structure analysis of the charge–discharge mechanisms of dithiobiuret polymer used as a high-capacity cathode material for lithium-ion batteries

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ABSTRACT

We investigated the electronic structures of low-molecular-weight dithiobiuret (DTB) compounds in both reduced and oxidized states along with those of a DTB polymer in the discharged and charged states using X-ray absorption near edge structure (XANES) measurements. DTB is a simple and lightweight organosulfur molecule with two neighboring tautomeric thiol/thione groups ($-\text{SH}/>\text{C}=\text{S}$) that can form disulfide (S–S) bonds by reversible oxidative cyclization. The DTB polymer, composed of alternating DTB and phenylene (Ph) units, exhibited a high capacity (about 260 mA h g^{-1}) without any significant degradation in the charge and discharge cycle characteristics. Based on XANES measurements, charge–discharge experiments, and quantum chemical calculations, we propose that the reactions of two types of redox couples contribute the redox reaction of the DTB polymer.

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1. Introduction

Lithium-ion batteries (LIBs) are one of the most promising energy storage devices owing to their high energy densities and capacities. However, for application in large-scale stationary energy storage as well as electric vehicles, further improvements in their capacities and lifetimes are required. Because the theoretical capacity of the cathode materials in commercial LIBs ($100\text{--}200 \text{ mA h g}^{-1}$) is much less than that of the anode material graphite (372 mA h g^{-1}), the development of new cathode materials is crucial [1–3]. Sulfur is a promising cathode material for next-generation lithium batteries because it has the highest theoretical capacity (1672 mA h g^{-1}) based on the conversion reaction of

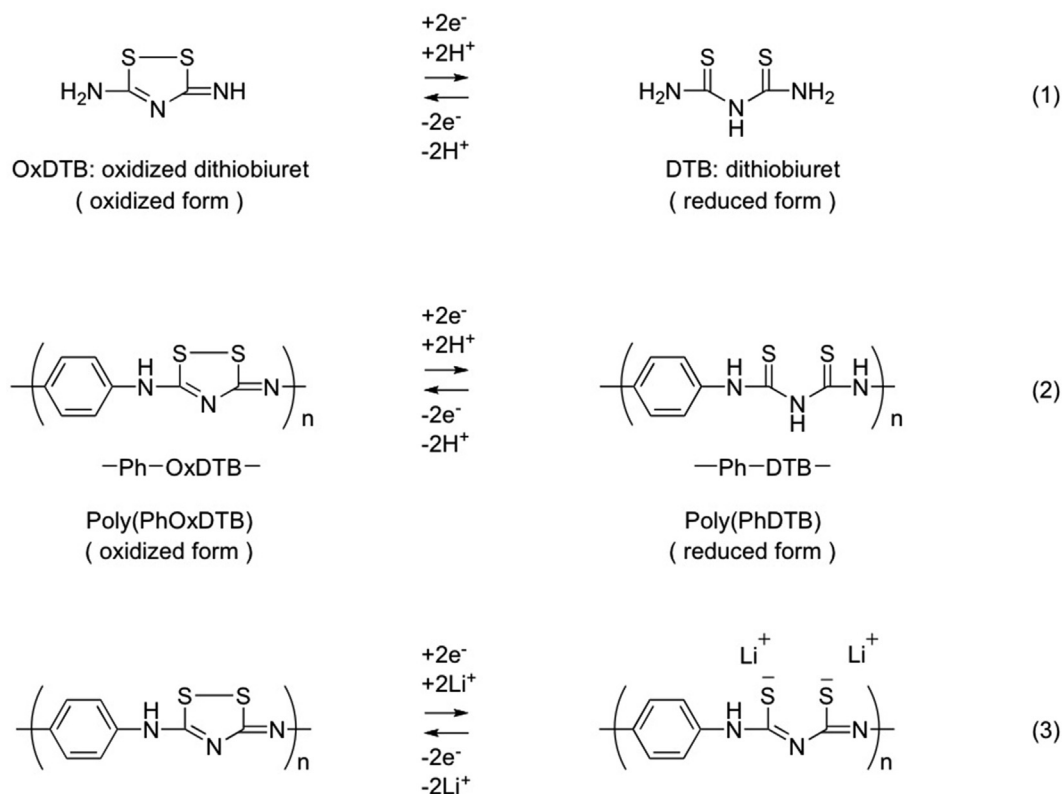
sulfur (S_8) to lithium sulfide (Li_2S) by disulfide (S–S) bond formation/cleavage. However, the intermediate lithium polysulfides (S_x^{2-}) formed during the conversion reaction are soluble in liquid electrolytes, resulting in capacity loss and cycle instability [4–6]. To solve the dissolution problem, two approaches have been proposed. The first is the entrapment of sulfur materials in host materials [7–13]. This approach, however, is not sufficient to prevent species from dissolving into the electrolytes [7–9,13]. The other is the use of S–S polymers, in which sulfur is covalently bound to a polymeric backbone [14–17]. These S–S polymers do not produce soluble intermediate lithium polysulfides, thus preventing capacity loss.

We previously reported the development of two types of S–S polymeric cathode materials [18,19]. One is a dithiobiuret (DTB) polymer, composed of alternating phenylene (Ph) and DTB units linked by nitrogen bridges (poly(PhDTB)) (Scheme 1(2)). DTB is a simple, lightweight molecule with two neighboring tautomeric thiol/thione groups ($-\text{SH}/>\text{C}=\text{S}$) [20,21]. DTB can form disulfide (S–S) bonds by reversible oxidative cyclization to form a five-membered ring, resulting in oxidized dithiobiuret (OxDTB) [22] (Scheme 1(1)). On the assumption that the charge–discharge

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Scheme 1. Schematic representation of the redox reactions of DTB and the DTB polymer. (1): The redox reaction of dithiobiuret (DTB, reduced form) and oxidized dithiobiuret (OxDTB, oxidized form). (2): The proposed redox reaction of the DTB polymer (poly(PhDTB), reduced form) and oxidized DTB polymer (poly(PhOxDTB), oxidized form). (3) The proposed charge–discharge reaction of a DTB polymer for lithium batteries.

reactions of the DTB units in a DTB polymer afford a high capacity (two-electron reaction per formula unit as shown in Scheme 1(3)), we synthesized this polymer that was denoted as “as-synthesized DTB polymer”. We found that in the charge–discharge cycles of the DTB polymer a high capacity of up to 260 mA h g^{-1} was achieved, which is consistent with the two-electron reaction per formula unit. We, however, have not clarified the reaction mechanism or the origin of the high capacity. In this report, we studied the valence changes of DTB units in the DTB polymer at discharged/charged states by *ex-situ* X-ray absorption near edge structure (XANES) measurements in comparison with low-molecular-weight DTB compounds in reduced/oxidized states.

2. Experiment

2.1. Materials

DTB and sodium borohydride (NaBH_4) were purchased from Tokyo Kasei Corp. (TCI). Tetrahydrofuran (THF), ethanol (EtOH), chloroform (CHCl_3), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), hydrogen peroxide (H_2O_2), iodine (I_2), sodium hydroxide (NaOH), hydrochloride (HCl), benzyl chloride (BnCl), and phenylthiourea were purchased from Kanto Chemical Co. *N,N'*-1,4-phenylenebisthiourea and 1,4-phenylene diisothiocyanate were purchased from Aldrich Chemical Co. A mix of 1 M lithium hexafluorophosphate (LiPF_6)/ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1 in volume) was purchased from Kishida Chemical Co. Polyvinylidene fluoride (PVDF) was purchased from Hosen Corp. All the chemicals purchased were used as-received without further purification.

2.2. Preparation of the low-molecular-weight DTB compounds

Oxidized dithiobiuret (OxDTB), *N,N'*-diphenyl-dithiobiuret (diPhDTB), oxidized *N,N'*-diphenyl-dithiobiuret (diPhOxDTB), and *S*-benzylated *N,N'*-diphenyl-dithiobiuret (diPh(SBn)DTB) were synthesized based on previously reported procedures [22–28]. OxDTB HCl was prepared by the oxidation of DTB with H_2O_2 in a mixture of EtOH and aqueous HCl at room temperature (Scheme 2(1)) [22]. *S*-Benzylated phenylthiourea (Ph(SBn)Tu) was synthesized by the benzylation of phenylene thiourea with BnCl in EtOH during reflux, followed by neutralization with NaOH (Scheme 2(2)). DiPh(SBn)DTB was synthesized by the addition of phenylene isothiocyanate to Ph(SBn)Tu in THF at reflux (Scheme 2(3)) [26]. DiPhOxDTB was synthesized by the oxidation of diPh(SBn)DTB with I_2 in CHCl_3 at reflux, followed by neutralization with NaOH (Scheme 2(4)) [23,24,26]. DiPhDTB was synthesized by the reduction of diPhOxDTB with NaBH_4 in THF–EtOH at room temperature (Scheme 2(5)) [27,28].

2.3. Preparation of the DTB polymer

The DTB polymer was prepared based on a three-step synthetic method reported in our previous work [18]. The first step was the synthesis of *N,N'*-1,4-diphenylene-bis(*S*-benzylthiourea), which was achieved via the benzylation of *N,N'*-1,4-phenylenebisthiourea (2 mmol) with BnCl (5 mmol) in EtOH (5 mL)/DMF (5 mL) at 70°C for 3 h, followed by neutralization with an NaOH solution (Scheme 3(1)). The second step was the polyaddition of *N,N'*-1,4-diphenylene-bis(*S*-benzylthiourea) (2 mmol) and 1,4-phenylenediisothiocyanate ($\text{Ph}(\text{NCS})_2$, 2 mmol) in DMAc (10 mL) at 80°C for 6 h to synthesize poly(Ph(SBn)DTB), the as-synthesized DTB

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