Preparation and Charge–Discharge Properties of a Novel Organosulfur Polymer, Poly(*p*-phenylene thiuret), for Battery Applications

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A new redox polymer consisting of benzene and thiuret, poly(*p*-phenylene thiuret) (PPT), is presented as a cathode material for lithium secondary batteries. The high capacity and cycleability are achieved by introduction of an S–S bond as a side group to a polymer. To prepare PPT, we synthesized a precursor polymer by a condensation of S-benzylthiourea with isothiocyanate and modified this polymer to PPT by an electrochemical reaction.

Recently, organosulfur compounds have been investigated as a cathode material for rechargeable lithium batteries with potentially very high capacity.[1–6] A disulfide (S–S) bond contained in these compounds is a key component for charge storage. When these compounds are incorporated into lithium batteries as a cathode material, the reduction of S–S bonds is associated with the insertion of Li ions and depolymerization of the polymer, while oxidation results in formation of polymer backbone. Theoretical charge capacity of these materials is possibly 2–3 times higher[1,2, 4–6] than those of other groups of materials, such as inorganic intercalation compounds and conducting polymers.

This group of compounds, however, has three disadvantages for battery application, namely, their slow redox rate at room temperature,[4,5] no electrical conductivity, and the solubility of low-molecular-weight monomeric units at the reduction process.[6] To overcome these disadvantages and to achieve higher capacity, we synthesized a new class of redox system based on organosulfur compounds consisting of dithiazolium and benzene that provides three one-electron reactions per unit. This system enhances the redox rate and produces conductivity by its π-conjugated system and restricts the solubility by introduction of S–S bonds as a side group to a polymer chain.[7]

In this paper, we report another attempts to reduce the solubility, which causes short cycle life and low charge capability for batteries, by synthesizing a new redox polymer with two electron reactions, involving S–S bonds as a side group.

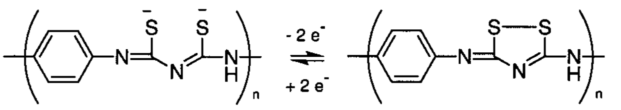
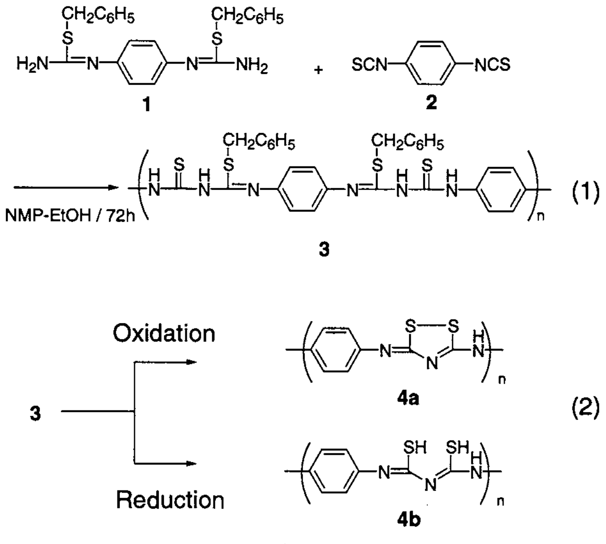


Figure 1. Concept of a redox reaction of PPT consisting of benzene and thiuret.

Figure 1 displays a redox reaction of the new polymer, poly(*p*-phenylene thiuret) (PPT), consisting of benzene and thiuret[8] (3,5-diimino-1,2,4-dithiazoline). At the reduced stage (the left side of Figure 1), thiol is attached as a side group to a main polymer chain. By oxidation of two electrons, a five-membered ring is formed resulting from the formation of the S–S bond (the right side of Figure 1). In this configuration, the scission and formation of S–S bonds are expected to be reproducible, since the S–S bond does not cause depolymerization, as encountered in the conventional organosulfur compounds. Although the redox ability of low-molecular thiuret compounds with the S–S bond has been already reported,[8–14] these compounds themselves are not suitable for practical applications for cathode materials because of their high solubility.

The theoretical charge capacity of PPT is estimated to be 259 mAh/g (based on the PPT's equivalent weight) assuming that PPT provides two electrons with the S–S reaction.

Scheme 1 shows synthetic procedures for PPT with two steps. The first step is a condensation of *N,N'*-1,4-phenylenebis(*S*-benzylthiourea) (**1**), which was synthesized from *N,N'*-1,4-phenylenebisthiourea and benzyl chloride following to the known procedure,[11,12] with phenyl 1,4-diisothiocyanate (**2**) to synthesize a precursor polymer (**3**) (Eq 1). The result of the elemental analysis (C, 61.05; H, 4.44; N,15.7%) of **3** was in agreement with the theoretical estimations ($C_{15}H_{13}N_2S_3$: C, 60.17; H, 4.38; N, 14.03%). The IR spectrum showed that **3** has peak at 3166 cm^{-1} originating from the NH stretching and also peaks at 1502 and 1222 cm^{-1} derived from N–C(=S)–N stretching.[15] These results are consistent with the molecular structure **3**.



Scheme 1.

The second step is the oxidative or reductive debenzylation for *S*-benzylthiourea of the precursor **3** to afford PPT (**4a** or **4b**) (Eq 2). To prepare PPT, we adopted an electrochemical reaction using a lithium battery with **3** as a cathode material. Complete debenzlylation is required for estimation of charge capacity of PPT. It is difficult, however, to get completely debenzlylated PPT by a chemical reaction, since **3** is an insoluble compound. An electrochemical reaction is superior to a chemical reaction in point of generation of completely debenzlylated PPT in heteroge-

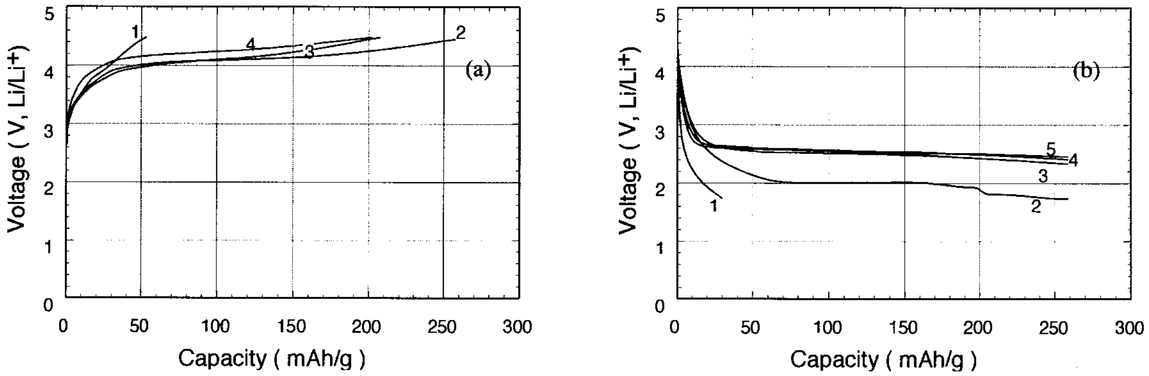


Figure 2. Charge(a) -discharge(b) curves of the Li/precursor **3** composite electrode battery at a 10 h rate as a functional of cycle number. The numbers shown are cycle numbers.

neous reaction and estimation of charge capacity for PPT. Exact charge capacity for PPT can be estimated from an amount of **3** introduced in a cathode. Hence, the execution of charge–discharge test for lithium batteries in this paper has two purposes: one is the synthesis of PPT and the other is the estimation of electrochemical ability of synthesized PPT. The charge–discharge test is not affected by the eliminated material, toluene, by debenzylation, since it diffuses away from an electrode.

The lithium battery was fabricated with the composite cathode containing **3** [44 weight percent (44%)], carbon (44%), and binder (12%), 1 M (M = mol dm^{-3}) LiClO$_4$/ethylene carbonate–diethyl carbonate electrolyte, and lithium as the reference and the anode. The charge–discharge test was performed at a 10 h rate, 0.07 mA cm^{-2}, (i.e., to complete a discharge in 10 h using the theoretical charge capacity of PPT, 259 mAh/g) between 1.75 and 4.5 V vs Li. The charge–discharge test, which starts with the discharge process, can be performed repeatedly, indicating that this polymer has an electrochemical activity. Figure 2 shows charge and discharge curves during five cycles.

The charge and discharge capacities of the first cycle were smaller and its voltage curves were steep. In the second cycle, the charge and discharge capacities came up to the theoretical value, 259 mA h/g, however, discharge curve was less flat than that of the subsequent cycles. From the first cycle to the third cycle, the discharge capacities increased and voltage curves were gradually flattened with increasing cycles. After the third cycle, discharge curves flattened around at 2.5 V with a capacity of 259 mA h/g, which came up to the theoretical value.

The charge–discharge behavior during the first three cycles provides a proof that PPT was synthesized from **3** in the cathode by the electrochemical reaction. During these cycles, the translation of capacity and curve shape can be explained that the irreversible debenzyl reaction of **3** changes the reversible S–S reaction of PPT. The constant discharge capacity after the third cycle, which is fair agreement with our assumption that the S–S reaction undergoes per polymer unit, is indicative of successful synthesis of PPT by the electrochemical reaction. The magnitude of discharge capacity, 259 mA h/g, is about 1.5–2 times higher than those of inorganic intercalation compounds and ordinary conducting polymers.

Furthermore, the reversible capacity after the third cycle exhibits that PPT has an S–S bond as a side group, which does not cause the depolymerization and that the cycle life for a lithium battery with PPT is extended. The high discharge capacity with good cycleability promises that PPT is a candidate for a high capacity cathode material.

Interestingly, at the end stage of discharge, battery voltage did not drop down. This results suggest that PPT has further redox ability derived from other redox moiety, namely nitrogen which connects dithiazolium and benzene. Voltage drops found at the beginning stage of discharge are possibly ascribed to the internal resistance of the cathode materials, which were not mixed uniformly, and the degree of contact for the collector and the cathode materials.

To conclude, we synthesized a new redox polymer consisting of benzene and thiuret, (PPT), as a high charge storage, 259 mAh/g, and extended cycleability cathode material for lithium secondary batteries. Introduction of an S–S bond as a side group to a polymer is crucial to obtain this high capacity and cycleability.

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