Photo-oxidation of an organosulfur for photo-charging of lithium-ion batteries

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Abstract. Polymers of organosulfur with S-S bonds are potential cathode materials for high-capacity lithium-ion batteries, and the photo-oxidation of organosulfurs can be applied in the future to the photo-charging of batteries. Herein, we present the photo-oxidation of dithiobiuret (DTB), a simple organosulfur molecule with two neighbouring tautomeric thiol/thione groups (-SH/>C=S) that can form a disulfide (S-S) bond by reversible intramolecular oxidative cyclization. Aqueous solutions of DTB with different pH values were irradiated by visible light from a halogen lamp. Photo-oxidation was confirmed by ultraviolet (UV) absorption spectroscopy, on comparison of the UV absorption spectra of DTB and chemically oxidized DTB. The rate of photo-oxidation depended on the pH of the DTB solution, and the highest photo-oxidation rate of ~ 2.8 × 10⁻³ min⁻¹ was observed at a pH of ~ 3.1.

1. Introduction
Lithium-ion batteries (LIBs) constitute a class of the most promising energy storage devices due to their high capacity. For application in large-scale stationary energy storage, as well as for electric vehicles, further improvements in terms of their capacity and lifetime are required. Since the capacity (100 – 200 mAh/g) of the cathodes in commercial LIBs is much less than that of the anode (graphite, 372 mAh/g), development of cathode materials is a crucial issue. In this context, sulfur-containing materials can be considered as cathode materials with higher capacity, due to the small atomic mass and wide range of valence states of sulfur. In fact, many organosulfur compounds have been investigated [1-10] in addition to the sodium-sulfur (NaS) battery for stationary applications. Among organosulfur compounds, 2,5-dimercapto-1,3,4-thiadiazole (DMcT) showed high capacity, > 300 mAh/g [5,6,8-10].

The origin of the high capacity of organosulfur materials lies in using the formation/scission of the disulfide (S-S) bond as the charge/discharge processes [8]. However, many issues need to be resolved for the application of sulfur-containing materials to consumer products, such as slow redox rate at room temperature [8,9], lack of electrical conductivity, and dissolution into the electrolyte solution during the discharge (reduction) process [10]. Uemachi et al.[11,12] designed and synthesized a type of organosulfur polymer with S-S bonds in the side group to address these concerns—polymers with the dithiobiuret (DTB) unit incorporated into the polymer backbone. The DTB unit possesses two neighboring tautomeric thiol/thione groups (-SH/>C=S) that can form an S-S bond by reversible intramolecular oxidative cyclization [11,12]. The developed materials show high electrical conductivity and low solubility in the electrolyte owing to their polymeric form. Moreover, they have...
potential for exhibiting high redox rates because the sulfur in the tautomeric thiol/thione groups can react with the neighboring sulfur in the same molecule. It is well known that the scission and formation of S-S bonds through redox reactions can be controlled by photo-irradiation [13-15]. Formation of the S-S bond by photo-oxidation, therefore, can be used for photo-charging the cathode of a lithium-ion battery with the abovementioned organosulfur polymers (DTB copolymers).

Recently, a highly efficient photo-charging lithium-ion battery [16] was reported based on a combination of solar cells and rechargeable batteries [17]. However, this kind of system has disadvantages such as bulkiness and complexity due to the combination of charging (solar cell) and storage (rechargeable battery) parts in the system. Direct photo-charging based on photoelectrochemical [18,19], ferroelectric [20], and other effects can solve these issues. Even in these cases, the efficiency of direct photo-charging batteries still needs to improve for practical applications [21-25]. Direct charging of a high-capacity electrode-material by photo-irradiation is, thus, the need of the hour. Photo-oxidation of the high-capacity cathode of DTB copolymers is promising, although a systematic study of these materials has not been reported so far. In this study, we investigated the photoreactions of DTB, a model monomer material of DTB copolymers for high-capacity LIBs, and succeeded in photo-oxidation (formation of the S-S bond) of DTB by irradiation of visible light as a proof of principle (Figure 1).

**Figure 1.** Schematic representation of redox reaction of DTB and the concept of photo-oxidation.

### 2. Experiments

DTB (CAS:541-53-7) was selected as a model sample, because it is one of the simplest organosulfur molecules. This small molecule is more appropriate than polymers, for light irradiation and UV absorption spectroscopy in aqueous solutions with a wide variation of pH. For photo-oxidation and UV absorption spectroscopy, 0.01 mM DTB was prepared in 200 ml of water. High-quality hydrochloric acid was used to control the pH of the solution. The pH of the solution was measured by a pH meter (Horiba D-75LAV).

A small volume of the sample solution (4 ml) was transferred to a quartz cuvette, and irradiated by visible light using a halogen lamp (Kenko Tokina Co., Ltd. KTS-150RSV), as shown in the inset of Figure 2. The incident light intensity at the sample position in this work was about 50 mW (~ 300 W/m²). UV absorption spectroscopy measurements were carried out using a system from ALS instruments (SEC2000-UV/VIS). Absorbance $A$ was calculated by

$$A = -\log\left(\frac{I}{I_0}\right),$$  

where $I$ and $I_0$ are the intensities of the transmitted light and incident light, respectively. In this work, the spectrum of pure water in a cuvette was taken as $I_0$ in order to subtract the large contribution of absorption by the cuvette and water. Temporal evolution of the UV absorption spectra by visible light irradiation was measured at the irradiation time ($t_i$) from 0 to more than 30000 min. When the aqueous solution of DTB is not connected to an electrochemical circuit (denoted as “open”), an effect of charging-up of solution may inhibit the oxidation reactions. In order to reduce such the effect, we also conducted the measurements under zero-voltage-bias application to the solution using an electrochemical circuit with a potentiostat from ALS instruments (DY2323) for removal of charging.
effect (denoted as “0 V bias”). For control experiments, chemically oxidized DTB was prepared. The chemical oxidation of DTB, i.e., formation of S-S bond in DTB, was confirmed by synchrotron radiation (SR) x-ray diffraction and SR x-ray absorption fine structure (XAFS) at the BL02B1 and the BL27SU beamlines of SPring-8, respectively [26,27].

Figure 2. (a) UV absorption spectra of DTB (blue solid curve) and chemically oxidized DTB (red dashed curve). (b) The UV absorption spectra of DTB at $t_i = 0$ min. (blue solid curve), 1120 min. (green dotted curve), and 11290 min. (red dashed curve), in aqueous solution at a pH of 4.5. Inset shows the setup for visible light irradiation by halogen lamp. Difference in the baseline of the three spectra in (b) may originate from the change in the background of the system during the long measurement time.

3. Results and discussion
The UV absorption spectra of DTB and chemically oxidized DTB [26,27] are shown in Figure 2(a), and a clear difference was observed. The spectrum of DTB can be represented by a linear combination of three Gaussian functions with peaks at 226, 256, and 282 nm, while that of chemically oxidized DTB can be represented by a linear combination of two Gaussian functions with peaks at 245 and 279 nm. A decrease in the peak intensity around 300 nm (282 nm in this work) [14,15] and the appearance of a peak at 245 nm are an indication of the oxidation of DTB. Figure 2(b) shows typical examples of the UV absorption spectra of an aqueous solution of DTB with a pH of 4.5, at $t_i = 0$, 1120 and 11290 min. for visualizing the temporal evolution of UV spectra. As $t_i$ increases, the typical peak of the
oxidized DTB at 245 nm increases in intensity. On the other hand, the main peak at 282 nm originating from DTB decreases.

The contributions of DTB and oxidized DTB to the UV absorption spectra at various $t_i$ were estimated by a linear combination of the spectra of DTB and chemically oxidized DTB. The intensities were normalized based on the intensity of DTB spectrum at $t_i = 0$ and the relative intensity of chemically oxidized DTB to DTB in Figure 2(a). Figure 3 shows the dependence of the normalized UV absorption intensities of DTB and oxidized DTB upon $t_i$ with/without light irradiation and with/without removal of charging effect at a pH of 6.4. The normalized intensity $I$ of DTB/oxidized DTB decreases/increases upon $t_i$, and can be expressed as

$$I = \exp\left(-\frac{t_i}{\tau}\right),$$  

$$I = 1 - \exp\left(-\frac{t_i}{\tau}\right),$$

with the time constants $\tau$, respectively. The $\tau$ which is inversely proportional to the reaction rate strongly depends on the experimental conditions: with/without light irradiation and with/without removal of charging effect. The $\tau$ values for data shown in Figure 3 are summarized in Table 1. It should be noticed that an increase in the intensity of the oxidized DTB spectrum corresponds to a decrease in the intensity of DTB spectrum at each pH, indicating that DTB is converted to oxidized DTB with an S-S bond through photo-oxidation. From these results, it can be concluded that the photo-oxidation of DTB efficiently occurs under light irradiation at 0 V bias application for removal of charging effect.

**Figure 3.** Visible light irradiation time ($t_i$) dependence of normalized UV absorption intensity of (a) DTB and (b) oxidized DTB with/without light irradiation (denoted as light/dark) and with/without removal of charging effect (denoted as 0 V bias/open).
**Table 1.** Photo-oxidation time constant $\tau$ for various experimental conditions at a pH of 6.4.

| Experimental conditions | $\tau$ (min) |
|-------------------------|--------------|
| With light irradiation (light) | $1.4 \times 10^3$ |
| Without removal of charging effect (open) | $4.9 \times 10^3$ |
| Without light irradiation (dark) | $2.6 \times 10^3$ |
| With removal of charging effect (0 V bias) | $5.3 \times 10^5$ |
| Without removal of charging effect (open) | $5.3 \times 10^5$ |

Figure 4 shows a relation between the photo-oxidation rate ($1/\tau$) of DTB and the pH value of the solution under light irradiation at 0 V bias application for removal of charging effect. The most efficient photo-oxidation rate, $\sim 2.8 \times 10^{-3}$ min.$^{-1}$, was achieved at the condition of a pH of $\sim 3.1$.

**Figure 4.** Photo-oxidation rate from DTB to oxidized DTB at 0 V bias application for removal of charging effect for various pH values.

**4. Conclusions**
We have succeeded in the photo-oxidation of dithiobiuret (DTB), a simple organosulfur molecule with two neighboring tautomeric thiol/thione groups (-SH/>C=S) that can form a disulfide (S-S) bond by reversible intramolecular oxidative cyclization. The abundance ratio of oxidized DTB increased with increasing visible light irradiation time. It was found that the photo-oxidation rate depends strongly on the experimental conditions, such as pH of the DTB aqueous solution and removal of charging effect. The highest photo-oxidation rate, $2.8 \times 10^{-3}$ min.$^{-1}$, was achieved at the condition of pH of 3.1 and 0 V bias application for removal of charging effect. For the application of photo-oxidation of DTB to photo-charging of lithium-ion batteries, further improvement of photo-oxidation rate and the demonstration of photo-oxidation of DTB copolymers in the cathode of LIBs are challenges for future research.
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