



Performance of nitrogen- and sulfur-containing carbon material derived from thiourea and formaldehyde as electrochemical capacitor

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ABSTRACT

In order to investigate the performance of an electrochemical capacitor consisting of a nitrogen- and sulfur-containing carbon material, the carbon material derived from thiourea and urea was synthesized by a polymerization process of the urea resin. No solid appeared after the polymerization process. When the dried sample after the polymerization process was heated in flowing N₂ gas, we obtained carbon material. However, there was no product when only thiourea was heated under the same conditions. The percentages of nitrogen and sulfur in all the samples synthesized from thiourea were roughly 5–20 wt.% and 3–8 wt.% even after washing with hot water, respectively. No specific peak derived from the redox reaction appeared in the CV graphs for the samples. The capacitance value of T-urea800W, which was synthesized by the heat treatment at 800 °C and then wash with hot water, was 138.8 F g⁻¹ at the current density of 50 mA g⁻¹ in a 1 M H₂SO₄ water solution whereas that value of a commercial activated carbon was 107.1 F g⁻¹ under the same conditions. It was presumed from the XPS measurements that the status of the nitrogen and sulfur in the materials are a pyridine-like nitrogen at the edge part of the graphitic structure, a quaternary nitrogen in the graphitic-layered structure, and S⁰, S⁴⁺, and S²⁻, respectively.

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1. Introduction

Recently, electrochemical capacitors, such as the electrical double layer capacitor (EDLC), have attracted much attention as energy-storage devices. Many research studies have been carried out to enhance the capacitance value of these electrochemical capacitors. Improvement of the electrode material is effective for the capacitance value. So far, some researchers reported that the addition of a heteroelement, such as N and P, is effective for improving the capacitance. It has already been reported that the nitrogen-enriched carbon material derived from the melamine form has a high capacitance value in a 1 M H₂SO₄ aqueous solution [1]. Moreover, some research studies about nitrogen-containing carbon materials have been performed for the development of a high performance material for electrochemical capacitors [2–4]. Jurewicz et al. reported the capacitance performance of the activated carbon derived from brown coal treated with urea [3]. Hsieh et al. reported the capacitance properties of amino-functionalized carbon nanotube/carbon paper [2]. Moreover, the effects of the nitrogen in the material have been discussed in these studies [5–8]. As for the addition of P, inorganic compounds, such as phosphoric acid, have been used as the P source [9,10] although in most of the studies phosphoric acid was used. The purpose of the addition was for activating the carbon material [9,10]. For the capacitance

properties of the materials containing sulfur, most of the research substrates were not a carbon material but a polymer [11,12]. Konno et al. reported the high performance of a capacitor made of a carbon material containing both boron and nitrogen, which was called a B(CN)⁻¹ composite [13].

We have recently reported that the carbon material derived from starch containing guanidine phosphate has a much high capacitance value related to the carbon material prepared from only starch [14]. The material contained both N and P in the structure. Therefore, co-doping of heteroatoms should be one of the promising approaches for the enhancement of the capacitance value.

Urea resin, which contains N atoms in the chemical structure, is synthesized from urea ((NH₂)₂CO) and formaldehyde. If thiourea ((NH₂)₂CS), which contains both the N atoms and the S atom in the structure, is used in place of urea, the synthesized resin should contain both nitrogen and sulfur in the structure. Therefore, if the heat treatment is performed on the resin synthesized from thiourea and formaldehyde, the synthesized carbon material must contain both nitrogen and sulfur in its structure. In this study, we attempted to synthesize the resin from thiourea and formaldehyde and investigate the performance of the carbon material derived from the sample as electrochemical capacitor.

2. Experimental

Fifteen grams of commercial thiourea (Wako Chemical) was mixed with 40 mL of formalin (Wako Chemical) at room temper-

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ature for ca. 10 min, and then 1 mL of concentrated sulfuric acid 1 was added in the solution and mixed for ca. less than 1 min at room temperature. The formalin solution mixed with thiourea was yellow. After the addition of conc. H_2SO_4 , the solution did not solidify. The product was dried at 80°C longer than overnight. The dried sample was used as the starting material for the carbon material prepared by the heat treatment. The dried sample was heated for 1 h in flowing N_2 (50 mL min^{-1}). The heating rate was ca. $20^\circ\text{C min}^{-1}$. The treatment temperature was 700, 800, and 900°C . The samples prepared at 700, 800, and 900°C are subsequently referred to as T-urea700, T-urea800, and T-urea900, respectively. When urea was used instead of thiourea for the polymerization process, the samples prepared at 700, 800, and 900°C are subsequently referred to as urea700, urea800, and urea900, respectively. The sample prepared from the commercial activated carbon was referred to as AC. The samples were washed with hot water (ca. 80°C) until the electrical conductivity of the filtrate reached to $5\ \mu\text{S}$. As for the samples washed with hot water "W" is added after the references, for example, T-urea700 \rightarrow T-urea700W. The powders were used for the BET and CHN-corder measurements. The powder prepared by the heat treatment, acetylene black, and teflon powder were mixed at the weight ratio of 8:1:1 to make the sheet. The sheet was cut ($20\text{ mm} \times 8\text{ mm} \times 0.5\text{ mm}$) and then used as the electrode for the electrochemical measurements, such as the cyclic voltammetric (CV) measurements and galvanostatic charge/discharge cycles. The CV measurements and galvanostatic charge/discharge cycles measurements were performed in a 1 M H_2SO_4 water solution, and a Pt plate was used as the counter electrode and the Ag/AgCl electrode was used as the reference electrode. A Pt plate was used as the collecting electrode. The electrical conductivity of the sheet samples was measured by the DC four-probe method. Other measurements were also performed (IR, XRD, XPS). As for the XPS, the peak position of $\text{Au}4f_{7/2}$ was used as the internal standard at 84.0 eV .

3. Results and discussion

3.1. Preparation process

During the first step of the polymerization process, commercial thiourea was mixed with formalin, and then 1 mL of concentrated sulfuric acid was added to the solution. After the mixing with conc. H_2SO_4 the samples remained liquid. On the other hand, in the case when urea was used instead of thiourea in the polymerization process, the solution changed to a solid. It is well known that the reaction conditions used in this study were effective for the polymerization of the urea resin. (This reaction condition is described in the textbook for high school chemistry.) Because the samples after the polymerization process were not solid but liquid, we cannot be convinced of the availability of this reaction condition for the polymerization of thiourea with formaldehyde. IR measurements were performed for the confirmation of the sample condition after the polymerization process. The IR spectra for thiourea (starting material) and the sample after the polymerization process are

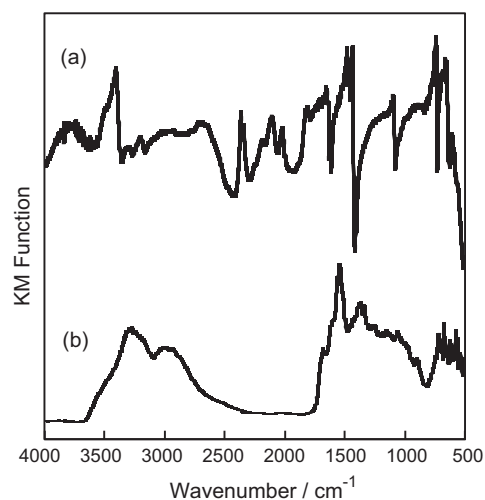


Fig. 1. IR spectra of the samples: (a) thiourea (starting material) and (b) the sample after the polymerization process.

shown in Fig. 1. The IR spectrum of the sample after the polymerization process was not the same as that of thiourea, which is the starting material of this process. The possible reasons for the change in the IR spectrum are (i) polymerization of thiourea with formaldehyde, and/or (ii) adsorption of formaldehyde on the thiourea.

Either way, the sample after the polymerization process contains both the N atoms and the S atoms. Therefore, the heat treatment during the carbonization was performed on the samples. The yields, which were defined as the weight of the sample after the heat treatment process per that of the sample before the heat treatment, are summarized in Table 1. The values of the samples prepared using thiourea are higher than those of the samples prepared using urea over the entire temperature range. In order to confirm the effect of the polymerization process on the synthesis of the carbon material, only thiourea was treated under the same conditions, that is, at 800°C for 1 h in flowing N_2 (50 mL min^{-1}). The yield was 0%, that is, there is no residue after the heat treatment. This result suggests that the polymerization process is necessary for the synthesis of the carbon material by the heat treatment. Moreover, this result may indicate that the polymerization reaction similar to the reaction of urea with formaldehyde occurred.

In order to estimate the percentages of the elements in the samples, measurements using CHN corder were performed. Moreover, as for the "T-urea", the percentages of the elements in the samples were calculated from the XPS measurements. The experimental results of the CHN corder and those of the XPS measurements are listed in Table 1 and Table 2, respectively. As for the data estimated by the CHN corder, we can presume that the "others" consists of O and S for the "T-urea" and contains O for the "urea" from the starting material components. Moreover, the percentages

Table 1
Yields, BET surface area, electrical conductivity, and the percentages of C, H, N, and others (measured by CHN corder) of the samples.

	Yield (%)	BET surface area ($\text{m}^2\text{ g}^{-1}$)	Electrical conductivity ($\Omega\text{ m}$)	C (wt.%)	N (wt.%)	H (wt.%)	Others (wt.%)
AC	–	1433	9.06	86.25	2.12	0.63	11.00
Urea700	4.4	194	0.21	69.71	14.84	1.95	13.50
Urea800	4.7	367	0.14	74.05	9.81	1.79	14.35
Urea900	1.6	1223	0.055	79.06	7.27	1.08	12.59
T-urea700	12.2	303	0.19	64.48	17.72	2.13	15.67
T-urea800	9.5	428	0.079	69.90	11.19	1.87	17.04
T-urea900	5.3	850	0.049	69.12	6.23	1.50	23.15
T-urea700W	–	81	0.21	65.23	18.95	2.02	13.80
T-urea800W	–	586	0.058	70.02	13.8	1.74	14.44
T-urea900W	–	490	0.080	80.75	9.11	1.32	8.82

Table 2

The percentages of C, N, O, and S (measured by XPS) on the samples.

	C (wt.%)	N (wt.%)	O (wt.%)	S (wt.%)
T-urea700	76.92	15.93	4.28	2.87
T-urea800	77.35	14.26	3.83	4.56
T-urea900	84.28	8.68	4.05	3.00
T-urea700W	73.66	16.84	5.87	3.62
T-urea800W	69.17	16.90	5.98	7.95
T-urea900W	81.54	10.37	3.93	4.17

should represent in whole, that is, not only surface part, but also the inside part, because of the measurement principle. As for the experimental data calculated from the XPS measurements, because the peak derived from the hydrogen atom cannot be measured, there was no percentage of hydrogen atoms. Moreover, the percentages should represent that of the near-surface of the samples because of the measurement principle. As for the results of the CHN corder, the value of “others” for the sample of “T-urea” increased with the increasing treatment temperature, and these values are greater than those of the “urea” samples. Moreover, the values decreased after the washing process. The percentages of “others”, which should be O and S, in the samples derived from thiourea are greater than those in the sample derived from urea. The values decreased after the washing process. Therefore, a substantial part of the residue after the heat treatment should be dissolve into the hot water. Especially, in the case of the sample treated at 900 °C, the degree of the reduction of “others” is high. The temperature dependence on the degree of the reduction could mean that the sulfur condition depended on the heat treatment temperature. After the washing process, the percentages of nitrogen in the “T-urea”s did not decrease, but instead slightly increased. Most of nitrogen could exist in the samples during the hot-water insoluble condition. As for the data from the XPS measurements, for all the “T-urea” samples the percentages of carbon decreased and those of the other elements such as N, O, and S increased with the washing process. This tendency conflict with the results of the CHN corder. The main reason for this difference could be that the CHN corder measures the entire part of the sample and the XPS measures near surface of the samples. From the results of both measurements, we can summarize as follows:

1. All the samples of “urea”, “T-urea”, and “T-urea W” contain nitrogen atoms and the percentages were roughly 5–20 wt.% even after the washing process.
2. The percentages of hydrogen atoms were *ca.* 2 wt.%.
3. The percentages of sulfur in all the samples of “T-urea” and “T-urea W” were roughly 3–8 wt.% even after the washing process. These summarizations should indicate that the synthesized samples contain both nitrogen atoms and sulfur atoms in the structure.

3.2. Electrochemical properties and characterization of samples

In order to evaluate the performance of the “T-urea” samples as an electrochemical capacitor, electrochemical measurements were performed. The experimental CV results measurements are shown in Fig. 2. All the graphs indicated that there was no peak related to the redox reaction. As for the “T-urea” and “T-urea W” samples treated at 700 or 800 °C, the graphs showed a peculiar shape regardless of the washing process, that is, a slight slope at the base and loose curve in the lower voltage potential on the upper side [15].

As an example of the data, potential-time curves (chronopotential graphs) of the T-urea800W are shown in Fig. 3. The IR drops of the graphs increased with the increasing value of the applied constant current. The capacitance values of the samples were calculated from the potential–time curves. The applied

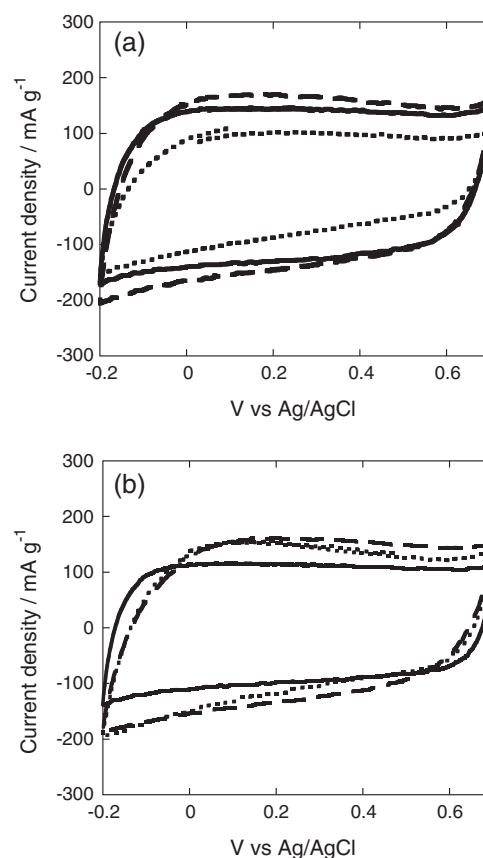


Fig. 2. CV graphs of the samples: (a) samples without the washing process and (b) samples with the washing process.

constant current dependence of the capacitance values calculated from the potential–time curves are shown in Fig. 4. Most of the values for the samples are greater than that for AC. The capacitance value decreased after the washing process except for the sample treated at 800 °C. The degree of the reduction with an increase in the applied current value was independent of the washing process. These results could mean that the structure, which affects the capacitance, depended on the heat treatment temperature.

The results of the BET measurements are listed in Table 1. The surface areas of the “T-urea”s increased with the increasing heat treatment temperature. This tendency was similar to the “urea” values. After the washing process, the surface area decreased except for the sample treated at 800 °C. In the washing process, we used paper filter for the filtration after the washing with hot water. At that time, some quantity of the sample clung to the paper filter. Therefore, we could not estimate the yield. The BET surface areas of T-urea700 and T-urea900 decreased after the washing process. Moreover, the percentages of others, which should be S and O, decreased after the washing process. Therefore, we can presume that the residue which consisted of S and O and which has higher surface dissolved into hot water. As for the T-urea800, the specific surface area increased after the washing process. This result should mean that the residue removed at the washing process has smaller specific surface area. Therefore, the condition of the residue could depend on the treatment temperature. The surface area values for the samples were much lower than that of the activated carbon (AC) except for the “urea900”. The values of the “T-urea800” and “T-urea800W”, which had the highest capacitance values, were 428 m² g⁻¹ and 586 m² g⁻¹, respectively. These values are much lower than that of AC although the capacitance values of “T-urea800” and “T-urea800W” were higher than that of AC. The

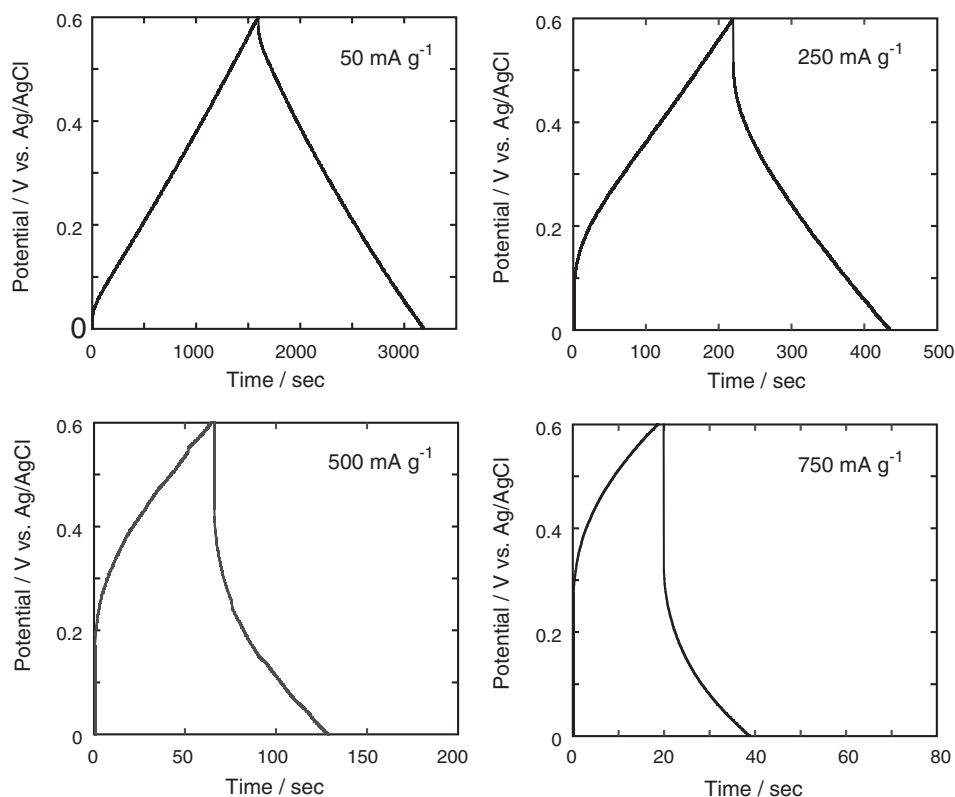


Fig. 3. Potential–time curves (chronopotential graphs) of T-urea800W.

capacitance value of the sample treated at 800 °C increased after the washing process in spite of the fact those of the other samples decreased after the washing process. The enhancement of the surface area by the washing process might be one of the reasons for the change in the capacitance value. However, we cannot explain the reason for the high capacitance values of the “T-urea” from the results of the BET measurements.

The highest capacitance value was achieved when the heat treatment temperature was 800 °C. In order to reveal the reason for the results, XPS measurements were performed on the “T-urea”. The XPS spectra for the samples are shown in Fig. 5. All the samples before and after the washing process had two peaks assigned to N1s in the spectra. The peak at ca. 400.8 eV should be assigned to the quaternary nitrogen, which is surrounded by three carbon atoms in the graphitic-layered structure. The peak at ca. 398 eV could be assigned to the pyridinic nitrogen, which exists at the edge part of the graphitic structure, or the nitrogen in the nitrile group [7]. The peak positions were independent of the washing treatment. It was reported that the quaternary nitrogen does not contribute to the enhancement of the capacitance value. As for T-urea700, the intensity of the peak at ca. 398 eV was higher than that at ca. 400.8 eV. As for T-urea800, the intensity of the peak at ca. 398 eV relative to that at ca. 400.8 eV decreased after the washing process. This result could mean that a part of the pyridine-like nitrogen or a part of the nitrogen in the nitrile group was removed during the washing process. As for the T-urea900, the intensity of the peak at ca. 398 eV was slightly lower than that at ca. 400.8 eV. These results could mean that the high ratio of the pyridinic nitrogen to the quaternary nitrogen decreased with the increasing treatment temperature. It was reported that the enhancement of the amount of nitrile group decreases the electrical resistivity [6]. The electrical resistivity of the T-urea800 slightly decreased after the washing process as shown in Table 1. Therefore, at least most of the removed nitrogen, which has a peak at ca. 398 eV, should be the

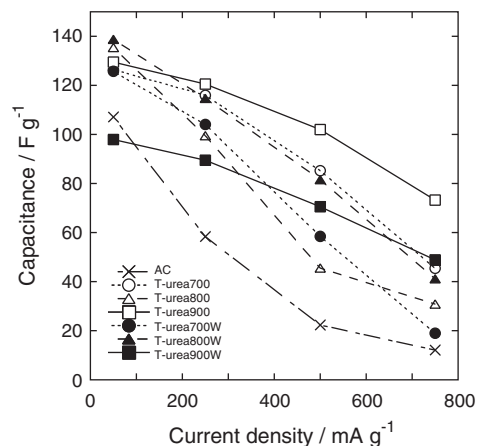


Fig. 4. Dependence of capacitance on current density of the samples.

nitrile group. It was reported that the pyridine-like structure could act as a pseudo-faradaic reaction site, resulting in the increased capacitance value. Therefore, we can presume that most part of the nitrogen assigned to the peak at ca. 398 eV should be the pyridine-like nitrogen.

As for the peaks related to the sulfur atoms, there are several peaks in the spectra. The broad peak at ca. 168 eV should be assigned to S⁴⁺. The peaks at ca. 164 eV and that at ca. 165 eV, which are assigned to 2p^{3/2} and 2p^{1/2}, respectively, could be derived from S⁰. These peak positions were independent of the washing process. As for T-urea800W, the peak assigned to S²⁻, which might be in the sulfide, appeared at ca. 162 eV. Ohno et al. reported that the peak derived from S²⁻ in thiourea appeared at ca. 162 eV [15]. In this study, thiourea was used as the starting material. However, there was no peak at

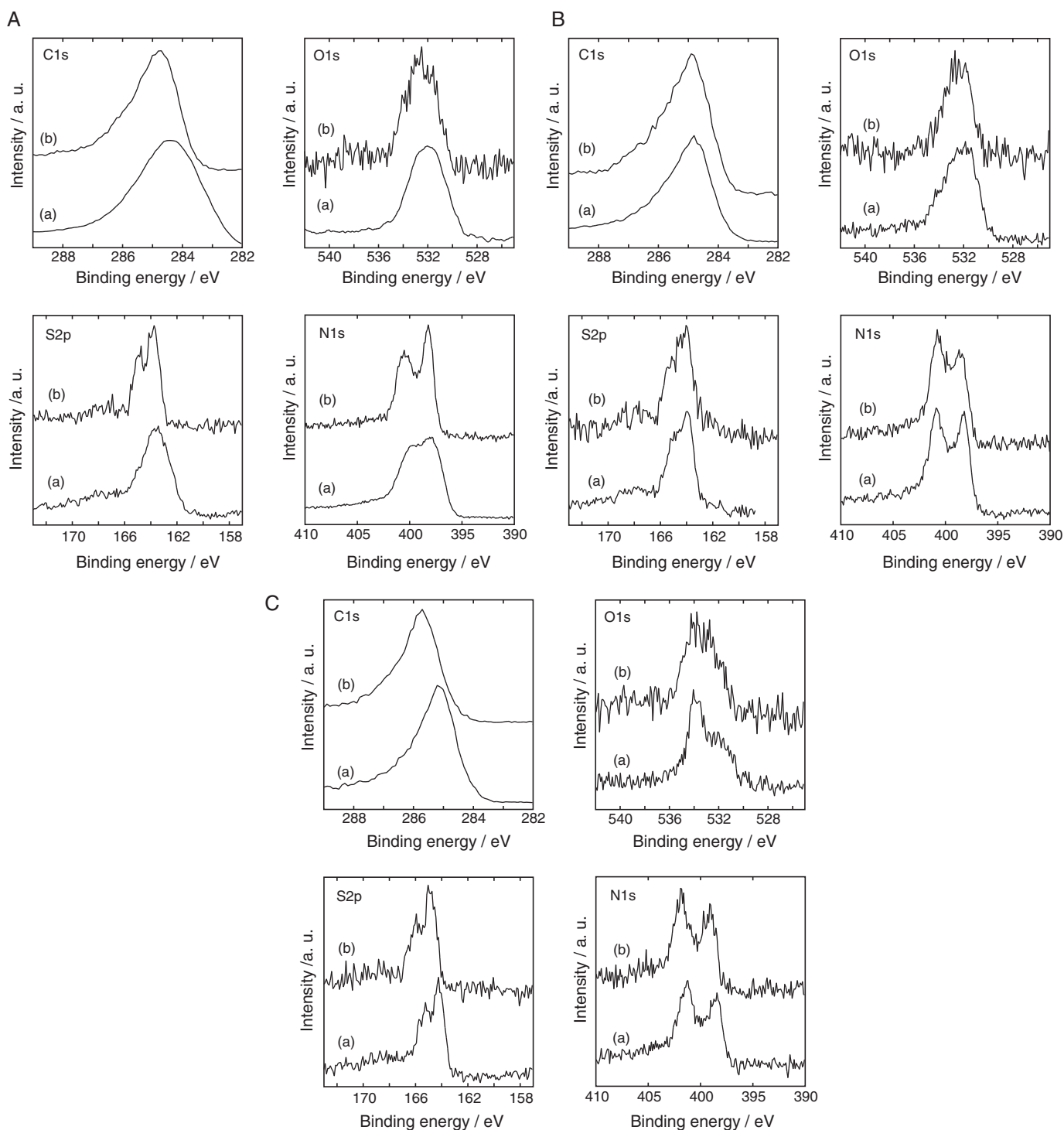


Fig. 5. (A) The XPS spectra of the samples treated at 700 °C: (a) before the washing process and (b) after the washing process. (B) The XPS spectra of the samples treated at 800 °C: (a) before the washing process and (b) after the washing process. (C) The XPS spectra of the samples treated at 900 °C: (a) before the washing process and (b) after the washing process.

ca. 162 eV in the spectra for the samples before the washing process. Therefore, even if the peak at ca. 162 eV was derived from thiourea, the thiourea was not the starting material but the product formed during the washing process. Fusalba et al. reported that the peaks of $S2p_{3/2}^{\sigma^-}$ and $S2p_{1/2}^{\sigma^-}$ appeared at 160.1 eV and 161.4 eV, respectively, for the electrochemically reduced poly(cyclopenta[2,1-b;3,4-b']dithiophen-4-one) film, which contains the S atoms in the structure [11]. They suggested that these peaks, which have a lower binding energy than the peaks assigned

to $2p_{3/2}$ and $2p_{1/2}$, indicated that some sulfur atoms are in a more negatively charged environment. Therefore, we can presume from the peak at ca. 162 eV for T-urea800W that some sulfur atoms are in a more negatively charged environment. The peak intensities for S^0 may slightly decrease after the washing process. Therefore, the sulfur in T-urea800 may change into S^{2-} .

The peak position of $Au4f_{7/2}$ was fixed at 84.0 eV as the standard for the peak positions of other peaks. As for T-urea700 and T-urea900, the position of C1s shifted to higher binding energy

after the washing process. On the other hand, as for T-urea800 there was no shift after the washing process. The tendency should be similar to the influence of the washing process on BET surface area. The difference of the residue may be the reason for the tendency.

The peak assigned to O sharpened after the washing process, and the peak position shifted to a higher binding energy, except for T-urea900. The change in the peak could be explained by the formation of sulfite. As for T-urea900, we noticed from the enhancement of the ratio of the noise intensity to the intensity of the signal that the peak intensity significantly decreased due to the washing process.

The summarized results are as follows:

N: pyridine-like nitrogen at the edge part of the graphitic structure, quaternary nitrogen in the graphitic-layered structure.

S: S^0 and S^{4+} (before washing process); for the T-urea800, a part of S^0 changes into S^{2-} (after washing process).

C: the structure frame of “T-urea” is stable against washing with hot water.

O: at least some of the sulfite is removed by the washing process.

The effect of nitrogen on the capacitance value was described on the basis of the reported papers because some papers reported the conditions and effects of nitrogen atoms in the carbon material. However, the effect of sulfur on the capacitance value was unclear because there is no report about the effect of sulfur in the carbon material on the capacitance value. Based on the experimental results of this study, we can suggest that the addition of sulfur (with nitrogen) to the carbon material could positively affect the capacitance value even if the effect is unclear at this point.

4. Conclusions

The performance as the electrode of an electrochemical capacitor using a carbon material derived from thiourea and formaldehyde was investigated. The polymerization process for the synthesis of the urea resin was used for the preparation of the samples in this study. In the case of only thiourea, that is, without the

polymerization process, no residue appeared after the heat treatment. On the other hand, when the sample was treated using the polymerization process, the carbon materials containing both N and S were produced after the heating process. The percentages of nitrogen and sulfur were estimated to be approximately 5–20 wt.% and approximately 3–8 wt.%, respectively. The capacitance values prepared from the thiourea “T-urea” and “T-urea W” were much higher than that of a commercial activated carbon in spite of the small specific surface area. The conditions of N, S, C, and O were investigated by XPS. The effect of the nitrogen on the capacitance was estimated based on previously reported studies. The effect of sulfur and the effect of the co-doping of sulfur with nitrogen were unclear at this time. However, the co-doping technique could be a promising method for the enhancement of the capacitance value.

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