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Journal

Journal of Materials Chemistry A, 5(44)

ISSN

2050-7488

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Publication Date

2017

DOI

10.1039/c7ta07522g

Peer reviewed

6 Understanding the function of cetyltrimethyl ammonium bromide 7 in Lithium/Sulfur Cells

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9 A surfactant material plays a significant role in creating a sulfur/carbon composite for lithium/sulfur cells. CTAB
10 (cetyltrimethylammoniumbromide) is a widely used surfactant material in various fields. In this study we identified the
11 functions of CTAB in a sulfur-graphene oxide composite used as the cathode material for lithium/sulfur cells, and the key
12 features for enhancing the capacity of the cells. The CTAB added in the synthesis procedure reacts with polysulfides during
13 the 155 °C heat treatment and produces cetylamine, cetylmethylamine, cetyldimethylamine, and dimethylpolysulfide as
14 products. Furthermore the composite produced by the reactions between cetyldimethylamine and sulfur cover the surface
15 of the sulfur. These work to enhance the performance of the cells. The findings presented here can be applied to various
16 kinds of sulfur/carbon composites to enhance the performance of the sulfur electrode.

17 Introduction

18 The research on lithium/sulfur cells with high theoretical
19 capacity has become one of the most active aspects of the
20 development of next-generation rechargeable batteries.
21 Lithium/sulfur cell technology is also attractive because sulfur
22 is a plentiful natural resource and low in cost. However, there
23 are still challenges in the practical application of
24 lithium/sulfur cells such as low sulfur utilization due to
25 sulfur's insulating properties and capacity degradation
26 resulting from dissolution-deposition or the polysulfide redox
27 shuttle phenomenon. Additional approaches to mitigate
28 these shortcomings of the lithium/sulfur cell are in high
29 demand.

30 To enhance the sulfur utilization in the cathode, a wide
31 variety of materials comprised of sulfur and various
32 conductive materials have been proposed.¹⁻¹⁸ Although a
33 number of methodologies have been researched, one major
34 method to make such composites is to infiltrate molten sulfur
35 into cavities of the conductive material by heating the
36 mixture above 155 °C.⁷⁻⁸ Another significant technique is
37 chemical deposition of sulfur on conductive materials.⁹⁻¹⁸
38 Since the chemical deposition of sulfur mostly takes place in
39 the solution phase, the conductive matrix should be
40 dispersed in the solution in advance. An aqueous system is

41 preferable from an environmental point of view for a scaled-
42 up system. In this case, usage of a surfactant is important to
43 disperse the conductive materials because many conductive
44 materials such as various kinds of carbon are not easily
45 dispersed in water. CTAB (cetyltrimethylammoniumbromide)
46 is a widely used surfactant material in various fields such as
47 medicine, household products, and nanoparticle synthesis
48 like porous silica. Also in battery materials research, CTAB has
49 been introduced to the sulfur/graphene oxide (S-GO)
50 composite as a surfactant.²⁻³ A similar substitute such as
51 tetradecyltrimethylammonium chloride has been used as a
52 surfactant to wrap sulfur particles by GO.⁷ In recent works,
53 the cell performance using a composite of S-GO has exhibited
54 a high initial discharge capacity of 1440 mA·h/g (sulfur) at
55 0.2C, and excellent rate capability up to 6C while still
56 maintaining high specific capacity (e.g., 800mA·h/g (sulfur) at
57 6C).¹ The cells demonstrated cycling performance up to 1500
58 cycles with a low capacity decay rate of 0.039% per cycle.¹ To
59 elucidate the reasons for such a high cell performance,
60 several types of analyses of the materials have been
61 performed.¹⁻⁶ The presence of C-S bonds and O-S bonds in
62 the S-GO have been observed by Raman spectroscopy, X-ray
63 Photoelectron Spectroscopy, Near-edge X-ray Absorption
64 Fine Structure, and X-ray Emission spectroscopy.³ In recent
65 work, it has been proposed that CTAB interacted with sulfur
66 not only as a surfactant but also as a protection layer to
67 enhance the cell performance because of the existence of C-S
68 bonds between sulfur and CTAB as shown by Raman
69 spectroscopy.¹

70 Although it has been reported that several bonds like those
71 mentioned above were created during the preparation
72 process and some effects enhanced the cycling stability of the
73 cell, the detailed effects of CTAB on the material preparation
74 and the cell performance have not been clarified. Not only for

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Electronic Supplementary Information (ESI) available. See
DOI: 10.1039/x0xx00000x

improvement of the S-GO materials, but also for application of CTAB to various new sulfur cathode materials, a deeper understanding of the chemistry of CTAB in the materials is indispensable. Also, the key factors for the high cell performance should be well understood for suitable scale-up of active material preparation and optimization of cell performance and lifetime. In this study, a whole series of characterizations and cell performance tests were conducted for the S-GO composites. The chemical reactions in the synthesis procedure of the S-GO cathode material have been elucidated by using TGA analysis, Raman spectroscopy, NMR spectroscopy and mass spectroscopy. To identify the peaks in the spectra, reference materials have been synthesized, and theoretical calculations were utilized. These results were used to clarify the effect of CTAB on the cell performance.

Experimental

Synthesis

We used the same method to synthesize all of the samples: 0.29 g sodium sulfide (Na_2S , anhydrous, Alfa Aesar) was dissolved in 12.5 mL distilled water to form a Na_2S solution. 0.36 g elemental sulfur (99.5%, Alfa Aesar) was dissolved in the Na_2S solution to form a sodium polysulfide (Na_2S_x) solution after stirring for 4 hours at 70 °C. 12 ml GO-water dispersion (4 mg/mL, Graphenea) was diluted by water to form 75 ml of suspension and sonicated for 1.5 hours. 82 mg CTAB (2.5 mM in the GO suspension, Sigma Aldrich) was dissolved in 3 mL water and added to the GO suspension drop-wise and stirred for 30 minutes and sonicated for 1 hour. Then, the Na_2S_x solution was added to the as-prepared GO-CTAB suspension drop-wise. The Na_2S_x -GO-CTAB mixture was stirred for 16 hours. Finally, the mixture was slowly added to 50 mL of 2 M formic acid solution (Aldrich) and the mixture was stirred for 3 hours, filtered, and washed with acetone and water. After drying at 45 °C in a vacuum oven for 12 hours, the sample was heated (heat treatment) in a tube furnace at 155 °C for 18 hours under the flow of Ar with a flow rate of 100 cc/min.

Table 1

	GO	Additives	Heat Treatment
S-GO		None	After the heat treatment
S-GO-BH		None	Before the heat treatment
S-GO-CTA0.625		0.625 mM CTAB	After the heat treatment
S-GO-CTA1.25		1.25 mM CTAB	After the heat treatment
S-GO-CTA1		1.0 mM CTAB	After the heat treatment
S-GO-CTA2		2.0 mM CTAB	After the heat treatment
S-GO-CTA2.5		2.5 mM CTAB	After the heat treatment
S-GO-CTA-BH		2.5 mM CTAB	Before the heat treatment
S-GO-CTA3		3.0 mM CTAB	After the heat treatment
S-GO-CTA4		4.0 mM CTAB	After the heat treatment
S-CTA	None	2.5 mM CTAB	After the heat treatment
S-CTA-BH	None	2.5 mM CTAB	Before the heat treatment
S-CA	None	CA	After the heat treatment
S-CMA	None	CMA	After the heat treatment
S-CDMA	None	CDMA	After the heat treatment
S-GO-CA		CA	After the heat treatment
S-GO-CMA		CMA	After the heat treatment
S-GO-CDMA		CDMA	After the heat treatment

The same procedure was performed to obtain S-GO composites containing different amounts of CTAB by changing the concentration of CTAB in the GO-CTAB suspension. The obtained samples are labeled as listed in Table 1. The material labeled as S-CTA was synthesized using the same procedure by using only a CTAB solution instead of a GO-CTAB suspension. Samples of the materials before the heat treatment are noted as –BH at the end of the sample label. The reference materials with amine species labeled as S-CA, S-CMA and S-CDMA were prepared by mixing sulfur and cetylamine (CA, $\text{C}_{16}\text{H}_{33}\text{NH}_2$), cetylmethylamine (CMA, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)\text{NH}$) and cetyldimethylamine (CDMA, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_2\text{NH}$), and heat treated under the same conditions as the S-GO composites. The other reference materials labeled as S-GO-CA, S-GO-CMA and S-GO-CDMA were prepared by mixing S-GO and the amines and heat treated under the same conditions as the S-GO composites. Dimethyl polysulfide (Me_2S_x) samples were synthesized as in the literature.¹⁹ 25 ml Na_2S_x aqueous solution was prepared using the same procedure as in the method for preparing the S-GO composite. The obtained solution was added into a mixture of methanol (35 mL) and methyl iodide (5 mL). The mixture reacted for 30 min at room temperature. Methanol and any remaining methyl iodide were evaporated under vacuum at 70 °C. Then water (25 mL) and dichloromethane (25 mL) were added and the organic layer was separated. Dichloromethane was evaporated under vacuum from the separated organic layer. The remaining yellow oily liquid was used as the reference material. Hydrogen polysulfides (H_2S_x) were synthesized according to reference.²⁰ 7 mL of sodium polysulfide solution was prepared using the same method as for the synthesis of the S-GO composite. The polysulfide solutions were slowly added into 30 mL of 6 M hydrochloric acid while stirring. After cooling the reaction mixture at 4 °C, the separated yellow oil was dissolved in 6 mL of carbon disulfide. The carbon disulfide phase was separated and dried.

Material characterization

Thermogravimetric analysis (TGA, TA Instruments Q5000) was used to determine the content of sulfur and the newly formed phase. A heating rate of 10 °C/min was used under the flow of N_2 with a flow rate of 100 cc/min. To determine the contents of each component in the materials, the weights of each component were calculated using the weight of the powder before the heat treatment as a reference. The contents of GO were determined by the weight of the remaining material at 600 °C for the before heat treatment sample. The contents of sulfur and Phase X produced during the heat treatment were calculated using the method graphically explained in Fig. S1. Raman spectroscopy (Horiba LabRAM ARAMIS) was used to investigate the interactions among GO, CTAB and sulfur. Mass spectroscopy was performed using a Fourier Transform Ion Cyclotron Mass Spectrometer coupled to a Linear Ion Trap (LTQ-FT) produced by Thermo Scientific. The solvent was

a mixture of 20% dichloromethane and 80% acetonitrile with a flow rate of 5 μ L/min. For NMR measurements, samples were dissolved in deuterated chloroform and were analyzed using a Bruker Avance II 900 MHz with TCI cryoprobe for ^{13}C NMR, and a Bruker Avance 500 MHz for ^1H NMR measurements. X-ray diffraction (XRD) was conducted using Bruker AXS D8 Discover GADDS X-Ray Diffractometer equipped with a Vantec-500 area detector and was operated at 35 kV and 40 mA at a wavelength of Co Ka, 1.79Å. S K-edge X-ray absorption spectroscopy (XAS) was conducted on BL5.3.1 and BL10.3.2 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). To eliminate the over-absorption effect, total electron yield (TEY) detection was used. The TEY signal was collected by monitoring the sample drain current. The energy ranges of the beamlines are from 2.4 keV to 12.5 keV, 2.4 keV to 5.0 keV and 2.1 keV to 17 keV, respectively. During the measurements, the energy scales for all XAS spectra were calibrated using elemental S spectra with a white line at 2472.20 eV. The theoretical calculations were performed by preparing the models for CTA⁺, CA, CMA and CDMA. The molecular geometries were first optimized and the Raman spectra were simulated for the geometries using density function theory (DFT) calculations. Each peak was represented by a Gaussian function with a maximum height proportional to the oscillator strength, using a full width at half maximum (FWHM) value of 5 cm^{-1} . The B3LYP exchange-correlation functional²¹ was utilized for DFT and the 6-31+G(d)²² basis sets were employed for the calculation. All calculations were performed using the Gaussian03 program.²³ SEM observation was conducted using Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope. A secondary electron detector was used.

Electrochemical characterization

The sulfur electrodes were fabricated by mixing the test materials, carbon black (Super C65) with a binder (SBR/CMC 1:1 by weight) at a weight ratio of 70:20:10 in isopropanol/water (1:3 by volume) solution to form a slurry. The resulting slurry was uniformly spread via a doctor blade onto pure aluminum foil. The solvent was allowed to evaporate at room temperature for 24 hours. The electrode was punched into circular pieces with a diameter of 12.7 mm for cell assembly. The electrodes were then dried in a vacuum oven at 50 °C for 24 hours to eliminate any solvent residue. The average sulfur loading of the electrodes was $\sim 0.8\text{mg}/\text{cm}^2$. For the electrolyte, 1 mol/kg lithium bis(trifluoromethylsulfonyl)imide (Sigma-Aldrich) in N-methyl-(N-butyl) pyrrolidinium bis(trifluoromethanesulfonyl)imide (Sigma-Aldrich) / 1,3-dioxolane / 1,2-dimethoxyethane mixture (2:3:3, by volume) was prepared and used for evaluation of the electrochemical performance. 0.5 mol/kg LiNO_3 was used as an additive in the electrolyte. CR2325-type coin cells were assembled with a separator (Celgard 2400) between a lithium metal foil (99.98%, Cyprus Foote Mineral) and a sulfur electrode fabricated with the S-GO or S-GO-CTA active material in a glove box filled with argon gas. Galvanostatic discharge and charge testing of the

coin cells was performed using a battery cycler (Maccor Series 4000) between 1.7 and 2.8V. The cell capacity was normalized by the weight of sulfur. All electrochemical characterizations were performed at 30 °C. Before all electrochemical characterizations, the cells were held at open circuit at 30 °C for 12 h.

Results and Discussion

It was found that S-GO-CTA having different amounts of CTAB showed different features in the TGA analysis. In Fig. 1 (a), the TGA results of S-GO-CTA having different amounts of CTAB are shown. From about 160 °C to 300 °C significant weight losses were observed, which is the typical weight loss for the evaporation of elemental sulfur (see Fig. S2). It can be noticed that as the amount of CTAB increased in the materials, the content of sulfur decreased and some portion remained even at 600 °C. At the same time, the TGA curve of S-GO-CTA-BH was almost the same as for S-GO. This result means that new reaction products were produced during the heat treatment of

Fig. 1 (a) TGA results of S-GO-CTA containing different amounts of CTAB, S-GO and S-GO-CTA before the heat treatment. (b) The change of the amount of each component in S-GO-CTA depending on the amount of CTAB calculated by the TGA results and the measurement of the weights of the samples before and after the heat treatment. (c) TGA results of reference samples prepared from sulfur and CA, CMA and CDMA.

the S-GO-CTA and the new phases were still present even at 600 °C. We call the new material Phase X. The changes of the total weights of the samples before and after the heat treatment were measured, and the contents of each component were calculated by the methods illustrated schematically in Fig. S1. The calculated contents are shown in Fig. 1 (b). The contents of all the components are indicated as the percentage of the total weight of the materials before the heat treatment. At first, we noticed that the total weight after the heat treatment decreased from the weight before the heat treatment, which means that something must have evaporated during the heat treatment. As the amount of CTAB increased, both the evaporated species and Phase X increased while the sulfur contents decreased. The amounts of GO were almost constant. These results mean that Phase X was produced by reactions involving sulfur and CTAB,

releasing some gaseous species. To identify Phase X, we review the reactions during the synthesis process. The flow chart of the synthesis process of the S-GO-CTA is shown in Fig. 2 (a). The reactions in the solutions during the synthesis were assumed to be as follows:

First, polysulfide solutions were made by adding sulfur to a sodium sulfide aqueous solution.

Second, an aqueous solution of CTAB (ionized into bromide anion and cetyltrimethylammonium cation (CTA^+ , $(\text{C}_{16}\text{H}_{33})(\text{CH}_3)_3\text{N}^+$)) was combined with an aqueous suspension of GO.

Fig. 2 (a) The flow chart of the synthesis process of the S-GO-CTA. (b) A graphical summary of the reactions taking place during the heat treatment.

After mixing the GO-CTAB suspension with the polysulfide solution, the polysulfide was acidified by decreasing the pH again using formic acid as shown in equation (3).

During the filtering and washing process, ions should be removed from the mixture, and S-GO-CTA-BH (-BH: before the heat treatment) remained after the washing process. From Equation (3), S-GO-CTA-BH was assumed to be a composite of sulfur, GO and CTA. But the exact structure of S-GO-CTA-BH was not clear, as was the case for S-GO-CTA after the heat treatment.

To identify Phase X, S-CTA was synthesized as a model material to examine the interaction between sulfur and CTAB without GO. In this case, the acidification process can be expressed by Equation (4)

S-CTA-BH might be a composite of sulfur and CTA⁺. And S-CTA-BH might change its chemical structure during the heat treatment to S-CTA.

To obtain information about the structure of S-CTA, ESI-MS spectroscopy was performed for S-CTA. The result showed only one peak that corresponded to cetyltrimethylamine (CMA,

$\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NH}$) with a mass of 256.3 (See Fig. S3).

Considering the mechanism of the ionization process in ESI-MS spectroscopy, only easily polarized molecules were detected in this method so that CMA was preferentially detected. Although there were possibilities for other species to be contained in S-CTA, the presence of CMA was confirmed by this experiment. By considering the structure of CTA⁺, CMA can be produced by removing two methyl cations from CTA⁺ and adding one proton as in Equation (5).

To examine the reaction between sulfur and CTAB during the 155 °C heat treatment, NMR spectra were obtained for S-CTA-BH and S-CTA. Fig. 3 shows ¹H NMR spectra of CTAB as reference, S-CTA-BH and S-CTA. In the spectrum of CTAB,

Fig. 3 ¹H NMR spectra of S-GO composite with and without CTAB, S-CTA before and after the heat treatment as model materials, and the spectra of CTAB and Me₂S_x as references.

peaks for H at the end of the chain of the cetyl group, methylene H in the middle of the chain, and methylene H adjacent to nitrogen in the chain appeared at 0.83 ppm, at 1.21 ppm, and 3.57 ppm respectively. The strong peak at 3.43 ppm was attributed to the H in the three methyl groups bonded to the nitrogen atom that could deshield the methyl group. Comparing the spectra of CTAB and S-CTA-BH we noticed that the peak for H in the trimethyl groups for S-CTA-BH moved to a lower shift from 3.57 ppm to 3.28 ppm. This movement suggested that the deshielding of the nitrogen

atom was weakened. Considering Equation (4), the sulfur atom might affect the chemical shift of the methyl H on the nitrogen by approaching the nitrogen atom. The peaks for H in the cetyl group at 0.83 ppm and 1.21 ppm moved slightly to 0.90 ppm and 1.27 ppm respectively. This movement might also be the result of interference of the sulfur atom near the nitrogen atom. The interaction between the sulfur atom and the nitrogen atom is also supported by the previous study which shows that the valence state of the sulfur was influenced by some interactions with CTAB in the sulfur-CTAB composite before the heat treatment.⁵⁻⁶ In the spectrum of S-CTA the peaks for H in the cetyl group were maintained at 0.90 ppm and 1.27 ppm, but the peak for the trimethyl groups disappeared. Instead several small peaks appeared from 2.5 ppm to 2.8 ppm. Considering the results of mass spectroscopy, which indicated the existence of CMA, the small triplet peak at 2.75 ppm can be attributed to the methylene H next to the nitrogen in cetylmethylamine. To identify the other unknown peaks in this region, we synthesized dimethylpolysulfides (Me_2S_x) as reference materials based on an assumption that polysulfide might react with methyl cations removed from CTA^+ considering Equation (5). Fig. 3 shows the ^1H NMR spectra of S-CTA and synthesized Me_2S_x and Fig. S4 shows the magnified spectra from 2.55 ppm to 2.8 ppm. The peaks for synthesized Me_2S_x at 2.59 ppm, 2.68 ppm, 2.717 ppm, 2.719 ppm, 2.721 ppm and 2.724 ppm can be identified for Me_2S_3 , Me_2S_4 , Me_2S_5 , Me_2S_6 , Me_2S_7 and Me_2S_8 , respectively.¹⁹ By comparing these spectra, it can be clearly seen that the peaks in the spectrum of S-CTA corresponded exactly to the peaks of Me_2S_x . These data show that S-CTA contains Me_2S_x as a result of the 155 °C heat treatment. ^{13}C spectra for S-CTA and Me_2S_x with the spectrum of CTAB are shown in Fig. S5, and the data show concurrence.

Combining the results from ESI-Mass spectrometry and NMR spectroscopy, the presence of CMA and Me_2S_x in S-CTA can be concluded. These experimental findings allow us to suggest the reaction during the heat treatment as Equation (6).

The boiling points of dimethylsulfide (Me_2S), dimethyldisulfide (Me_2S_2) and dimethyltrisulfide (Me_2S_3) are 37.3 °C, 110 °C and 170 °C, respectively. The boiling points of the other Me_2S_x having more sulfur atoms than three are higher than 170 °C. Regarding the temperature for the heat treatment as 155 °C, Me_2S and Me_2S_2 should be evaporated during the heat treatment. This fact corresponds with the NMR results that showed only Me_2S_x having more than three sulfur atoms. This result reminds us that some gaseous species which were produced by the reaction of CTAB should be evaporated during the heat treatment as shown in Fig. 1 (b). The evaporated species can be assumed to include Me_2S and Me_2S_2 considering the boiling points and the temperature of the heat treatment. Equation (6) helps us to suggest the structure of S-CTA-BH. After one CTA^+ coupled with one hydrogen polysulfide anion (HS_x^-), these two ions could be stabilized together in the solution and become S-CTA-BH. This assumption corresponds with the NMR result of S-CTA-BH in which the peaks for CTA^+ were maintained but shifted by the effect of polysulfide.

The NMR spectrum of S-GO-CTA containing GO is included in Fig. 3. S-GO-CTA showed the same peaks as S-CTA at around 2.7 ppm for Me_2S_x , at 1.27 ppm for methylene H and at 0.9 ppm for methyl H in CMA. The results mean that the same chemical reaction expressed as Equation (6) occurred in the process for S-GO-CTA as well as S-CTA. But the peaks for Me_2S_7 and Me_2S_8 were intensified, while Me_2S_3 and Me_2S_4 disappeared. Shorter polysulfides are assumed to be oxidized to longer polysulfides by the surface functional groups on GO in the mixture of GO and the polysulfide solution. The peak at 1.58 ppm in the spectra of S-CTA, S-GO-CTA and S-GO is caused by the H in water (see Fig. S5).²⁶ It was confirmed that there was no polysulfane (H_2S_x) in the material by checking the NMR spectra of synthesized H_2S_x (see Fig. S5).²⁴⁻²⁵ The spectrum of S-GO without CTAB is shown in Fig. 3. In that spectrum there is no peak other than the peak of water at 1.58 ppm. This absence of the peaks in the spectrum of S-GO supports the fact that CTAB is necessary for the reactions producing CMA and Me_2S_x . The peak at 2.2 ppm is for the H in acetone, which remained after the washing process of the material (see Fig. S6).²⁶

We have found that Me_2S_x and CMA were produced by the chemical reactions between polysulfide and CTA^+ during the heat treatment. Considering the reaction between polysulfide and CTA^+ as described in Equation 6, it is highly possible for cetyldimethylamine (CDMA, $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_2$) and cetylamine (CA, $\text{C}_{16}\text{H}_{33}\text{NH}_2$) to be produced during the heat treatment as well as CMA, because the difference among those species is only the number of the methyl groups on the nitrogen atom. The assumption of production of CDMA is also supported by the literature.²⁷ Now candidates for Phase X are Me_2S_x , CA, CMA and CDMA. If some of them are Phase X, they should be stable above 300 °C in the TGA analysis. But none of them was stable above 300 °C as shown in Fig. S2. This means further reactions were required to produce Phase X.

Assuming that Phase X materials are created by reactions involving sulfur and CA, CMA and CDMA, reference materials were prepared by the heat treatment of mixtures of sulfur and CA, CMA and CDMA, and labeled as S-CA, S-CMA, and S-CDMA, respectively. The TGA results for those model compounds are shown in Fig. 1 (c). All of them showed phases that remained even above 300 °C. This result strongly suggests the possibility that sulfur reacted with these cetylamine compounds that were produced by reactions between CTA^+ and polysulfide during the heat treatment, and produced Phase X. Furthermore, we prepared model compounds by adding CA, CMA and CDMA to S-GO and treated them by the same heat treatment. These compounds are labeled as S-GO-CA, S-GO-CMA and S-GO-CDMA as listed in Table 1. The TGA results of these model compounds are shown in Fig. 1 (c) as well. They showed stable features even above 300 °C, too.

In order to confirm whether some of S-CA, S-CMA, S-CDMA are Phase X, Raman spectroscopy was conducted. At first the spectra of S-GO-CTA and S-GO were compared in Fig. 4 (a). In the spectrum of S-GO, there are peaks attributed to sulfur at 150 cm^{-1} , 218 cm^{-1} and 470 cm^{-1} , and two broad peaks for GO at 1330 cm^{-1} and 1590 cm^{-1} , which are attributed to the D band and G band of carbon respectively. The spectrum of S-GO-CTA-BH was almost the same as that of S-GO. On the other hand, S-GO-CTA showed a quite different spectrum

from those spectra. No peak was found for sulfur, and new peaks at 490 cm^{-1} , 1037 cm^{-1} , 1255 cm^{-1} , 1425 cm^{-1} and 1520 cm^{-1} were found instead. Those peaks are labeled as peak A, peak B, peak C, peak D and peak F respectively. The D band and G band remained, overlapping with those new peaks. These results indicate that new phases having these peaks were produced during the heat treatment. Sulfur should be still inside the material even after the heat treatment judging from the results of TGA in Fig. 1 (a), and XRD patterns in Fig. S7. So, the fact that peaks for sulfur disappeared suggests that the newly produced phases covered the surface of sulfur in the composites. Although it was suggested that a peak at 636 cm^{-1} was evidence of C-S bonds in the previous study,³ the peak at 636 cm^{-1} was very small. So, in this study it is better to focus on the more prominent peaks as represented by peaks from A to F rather than the peak at 636 cm^{-1} . The Raman spectrum of the powder remaining after TGA analysis is shown in Fig. 4 (a). Interestingly this spectrum was almost the same as the

Fig. 4 (a) Raman spectra of the S-GO composite with and without CTAB, S-GO-CTA before and after the heat treatment, the powder remaining after TGA analysis of S-GO-CTA, and the spectra of sulfur and GO as references. (b) Raman spectra of the model compounds, S-GO-CA, S-GO-CMA, S-GO-CDMA and S-CDMA as references.

spectrum before the TGA analysis. The only difference was that the peak position of peak D slightly changed to 1439 cm^{-1} . Observing carefully the spectrum of S-GO-CTA, peak D had a shoulder at 1439 cm^{-1} . So, it can be mentioned that peak D disappeared after TGA analysis, and then the peak at 1439 cm^{-1} , which existed even before TGA analysis, just became clear. This peak at 1439 cm^{-1} is labeled as peak E. From these results, it can be said that the new phases having peaks A, B, C, D, E and F were produced during the heat treatment, and a part of the material having peaks A, B, C, E and F remained after TGA analysis as Phase X. The Raman spectra of the

model compounds, S-GO-CA, S-GO-CMA and S-GO-CDMA, were measured and are shown in Fig. 4 (b). Comparing the spectra between Fig. 4 (a) and Fig. 4 (b), S-GO-CDMA showed exactly the same spectrum as S-GO-CTA. Although S-GO-CMA showed quite a similar spectrum to those, peak D was not as clear as in the spectrum of S-GO-CTA. These results suggest that Phase X was created by the reaction between sulfur and CDMA during the heat treatment. The spectrum of S-CDMA, the model compound without GO, is shown in Fig. 4 (b) as well. Although the spectrum was almost the same as that of S-GO-CDMA, the existence of peaks B and C was not clear. And it was found that the samples were much more fragile under the laser beam for Raman spectroscopy than S-GO-CDMA. Actually, the spectra of S-CA and S-CMA could not be obtained easily because they were too unstable under the laser beam. These results suggest that GO stabilized these compounds made by the reactions between sulfur and CA, CMA, and CDMA. And peaks B and C appeared as the result of the interactions with GO. Considering the fact that the spectrum of S-GO-CA did not show peaks B and C clearly, and that peaks B and C for S-GO-CMA were smaller than S-GO-CDMA, it can be said that CA and CMA had less interaction with GO than CDMA. This can be a reason that S-GO-CDMA preferentially formed in the material. To identify the exact structure of Phase X, mass spectroscopy was conducted for S-CDMA. The results indicated the existence of two molecules. One had a formula of $\text{C}_{18}\text{H}_{38}\text{NS}$ with 300 m/z and the other one had a formula of $\text{C}_{33}\text{H}_{68}\text{NS}$ with 510 m/z . The spectra and the corresponding isotope patterns are shown in Fig. S8. Considering the structure of CDMA, the highly possible structure for $\text{C}_{18}\text{H}_{38}\text{NS}$ is $(\text{C}_{16}\text{H}_{33})(\text{CH}_3)\text{NCH}_2\text{SH}$, Cetylaminomethanethiol (S-CDMA-1), which can be created by one sulfur atom addition to a methyl group on the nitrogen atom in CDMA as shown in Equation (7). And the formula $\text{C}_{33}\text{H}_{68}\text{NS}$ can be $(\text{C}_{16}\text{H}_{33})\text{NH}(\text{CH}_2\text{SC}_{16}\text{H}_{33})$, N-cetyl-1-cetylsulfanylmethanamine (S-CDMA-2), which can be produced by addition of the cetyl group to the sulfur atom in S-CDMA-1 and removal of a methyl group from the nitrogen as shown in Equation (8).

These big molecules appeared on the surface of the S-GO composite after the heat treatment and stayed even above 300°C in the TGA analysis as Phase X. These results correspond with the suggestions in previous studies, which claimed that C-S bonds should be newly created between sulfur and CTAB.^{1, 5-6} Also the results are consistent with S K-edge XAS spectra of S-GO-CTA which showed an increase of intensity of the peak attributed to C-S bonds as the amount of CTAB increased (see Fig. S9). The peak assignments were discussed in detail in the reference⁵⁻⁶. A graphical summary of the reactions taking place during the heat treatment is shown in Fig. 2 (b).

The Raman spectra were examined again by considering the fact that S-CDMA-1 and S-CDMA-2 were the origins of specific Raman peaks. The spectra of the CTAB, CA, CMA and CDMA are collected in Fig. S9 as reference. All of them showed significant peaks around 1439 cm^{-1} and 1462 cm^{-1} . These

peaks became broader in the order of CTAB, CA, CMA and CDMA. The theoretical spectra of CTA⁺, CA, CMA and CDMA were calculated by using optimized models and are shown in Fig. S10 with their vibration modes. Although some differences between experimental and calculated spectra in the Raman shift were observed in the high wave number region, most of the peaks in the experimental spectra corresponded to the peaks in the calculated spectra. By comparing with the calculated spectra, the vibration modes of the peaks in the experimental spectra were analyzed. In all cases, the peaks centered at 1060 cm⁻¹ and 1127 cm⁻¹ corresponded to C-C stretching vibrations; the small peak centered at 1170 cm⁻¹ represented a C-N stretching vibration in the amine group; the peaks centered 1295 cm⁻¹, 1439 cm⁻¹ were attributed to C-H bending vibrations; and the peak at 1462 cm⁻¹ corresponds to CH₃ bending vibrations in the amine group. Considering the fact that S-CDMA-1 and S-CDMA-2 also have a common structure with CA, CMA and CDMA, peak D can correspond to a bending vibration of C-H bonds in the whole molecule, and peak E can correspond to the bending vibration of CH₃ in the amine group. In the previous study, it was mentioned that the peaks centered at 748 cm⁻¹ and 1040 cm⁻¹ represented C-S and O-S bonds, and 1260 cm⁻¹ and 1440 cm⁻¹ corresponded to C-H stretch vibrations respectively.³ However, from the knowledge gained from the calculated spectra and the results of mass spectroscopy, it can be said that the peaks at 748 cm⁻¹ and 1040 cm⁻¹ correspond to C-C or C-N stretching vibrations, and the peaks at 1260 cm⁻¹ and 1440 cm⁻¹ are for C-H bending vibrations.

The morphologies of S-GO, S-GO-CTA0.625, S-GO-CTA1.25 and S-GO-CTA2.5 were investigated. The SEM images are shown in Fig. S12. As the amount of CTAB increased, the surface morphology of the materials became flaky structure, while bulky morphology was observed in S-GO. Comparing the morphologies before and after the heat treatment, the main features of the morphologies were maintained. This means that the morphologies of the composites were largely determined by the process before the heat treatment by the effect of CTAB. When attentions are focused on the morphology before the heat treatment, among the GO flakes, morphology like that of a honey comb can be seen. These are the sulfur particles of which the surface was damaged by the electron beam of the SEM. The actual sulfur particles were not just rough surface and immediately started to become like a honey comb after focusing the SEM. Even though the parameters for the measurement were adjusted, some damage could not be avoided to get clear images. Just what was noticed about the difference before and after the heat treatment was that the sulfur parts were not fragile against the electron beam for SEM observation after the heat treatment anymore. This is supposed that Phase X protected the sulfur against the electron beam. Thus, this result supports that Phase X was created on the surface of sulfur particles.

To make clear the effects of Phase X in the materials on the electrochemical performance, cell tests were performed using the materials with different amounts of CTAB and without CTAB. These samples were controlled to contain the same sulfur content. Voltage profiles of S-GO, S-GO-CTA2.5, S-GO-CTA1.25 and S-GO-CTA0.625 in the tenth cycle at a C rate of 0.2 for discharge are shown in Fig. 5 (a). As shown in

Fig. 1 (b), the content of Phase X in S-GO-CTA3 was almost 10%, which was so much that it sacrificed the sulfur content in the cathode resulting low energy density. Therefore, S-GO-CTA2.5 was compared as a cathode material as having the highest concentration of CTAB. It is noticeable that although the capacities of the first plateau were almost the same in all of them, the capacities corresponding to the second plateau showed differences among the materials. S-GO-CTA2.5 showed highest capacity and the capacity in the second plateau decreased as the amount of CTAB decreased. S-GO showed the least capacity among them. The reactions in the second plateau involve mainly reduction of Li₂S₃ to Li₂S₂ and Li₂S.²⁸ Since the solubility of Li₂S is quite low, solid Li₂S deposits on the cathode during the discharge. The difference of the capacity in the second plateau among the materials having different amounts of CTAB suggests that Phase X encourages the uniform production of Li₂S on the surface of GO by interacting with Li₂S, and preventing significant agglomeration of Li₂S which can induce premature blocking of further conversion of polysulfide to Li₂S. Another possibility is that Phase X enhanced the wettability of Li₂S by the electrolyte solution so that the Li₂S does not agglomerate.

Fig. 5 (a) Voltage profiles of S-GO, S-GO-CTA0.625, S-GO-CTA1.25 and S-GO-CTA2.5 in the tenth cycle at a C rate of 0.2 for discharge. (b) The results of rate capability tests of S-GO, S-GO-CTA0.625, S-GO-CTA1.25 and S-GO-CTA2.5. (c) Voltage profiles of S-GO-CTA2.5 at

different C rates. The C rates for discharge and charge are indicated on left side and right side of the slash respectively for (b) and (c).

On the other hand, when there is no CTAB, Li_2S deposits inhomogeneously or agglomerates, then further reaction of polysulfide to form Li_2S might be blocked due to a lack of electronic conductivity. It can be assumed that the cross-linked long molecule structure of S-CDMA-2 stabilized the effects of Phase X as a facilitator of polysulfide reactions at the interface. The capacity decreased from first cycle to 4th cycle and increased from 5th cycle to 10th cycle in S-GO-CTA2.5, S-GO-CTA1.25 and S-GO-CTA0.625. This phenomenon was considered to be appear because the surface of the materials became wet more by the electrolyte solution after fifth cycle while the amount of active sulfur was lost gradually. By considering that the phenomenon was more significant when CTAB concentration was high and it did not appear in S-GO, Phase X took more time to be wet than sulfur. This is understandable when Phase X was intimate with Li_2S which has high polarity. The results of rate capability tests are shown in Fig. 5 (b). All of the materials showed high rate capability. The materials maintained the capacities in the same order of the amount of CTAB except in 2C discharge and 4C discharge for S-GO-CTA1.25. As the voltage profiles at different C rate for S-GO-CTA1.25, S-GO-CTA0.625 and S-GO were shown in Fig. S14, the overvoltage became bigger in the same order with C rate in S-GO-CTA1.25, the overvoltages were similar with those of S-GO-CTA0.625 though. These rate capability results suggest that Phase X did not contribute to the rate capability significantly because the materials having CTAB did not show a big advantage compared to S-GO without CTAB. The voltage profiles of S-GO-CTA2.5 at different C rates are shown in Fig. 5 (c). The capacity loss induced by high C rates was caused by the capacity loss in both the first plateau and the second plateau. As suggested in Fig. 5 (a), the advantage of having CTAB in the material is the capacity in the second plateau. Considering these results, the rate capabilities are apparently influenced by different factors than Li_2S distribution for example ion conductivity. Then the similar performance at 4C discharge in S-GO-CTA1.25 and S-GO-CTA0.625 can be caused by the ion conductivity. The ion conductivity and the wettability of Phase X will be investigated in other studies.

Conclusions

We have successfully identified the chemical reactions taking place during the synthesis process of S-GO-CTA and the key components for enhancing the capacity of cells using S-GO-CTA as a cathode material. The CTAB added in the synthesis procedure of S-GO-CTA reacts with polysulfide composite during the 155 °C heat treatment and produces Me_2S_x , CMA and CDMA. Furthermore, CDMA reacts with sulfur and creates S-CDMA-1 and S-CDMA-2 composing new stable materials, Phase X. The newly produced Phase X by the reaction of CTAB during the synthesis apparently worked as a promoter of the conversion reaction from polysulfide to Li_2S . Considering these effects of CTAB on the capacity enhancement, CTAB worked as both surfactant and the precursor of the functional layer. These new findings can be

applied for various sulfur-carbon composites for cathode materials in sulfur cells. These findings can also be applied to the control of the scaled-up production of the materials.

Acknowledgements

We thank Tevye Kuykendall of the Molecular Foundry of LBNL for his generous support. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

We appreciate helpful discussions with Yoon Hwa and Min-Kyu Song (now at Washington State University) of LBNL. We thank Jeffrey Pelton of the 900 MHz NMR Facility for his support. Funds for the 900 MHz NMR spectrometer were provided by the NIH through grant GM68933. We thank Rita V. Nichiporuk of the Quantitative Biosciences (QB3) institute at University of California Berkeley for her support.

We appreciate the experimental support from Yifan Ye, Jinghua Guo, Matthew Marcus and Jun Feng at the ALS. The work at the ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

We thank Graphenea for providing GO suspensions.

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