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Kawase, A

Cairns, EJ

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Method for creation of fine sulfur particles with graphene oxide for Lithium/Sulfur Cells

Ayako Kawase^a and Elton J. Cairns^{a,b}*

a. Energy Storage and Distributed Resources Division, Lawrence Berkeley
National Laboratory, Berkeley, CA 94720, USA

b. Department of Chemical and Biomolecular Engineering, University of
California, Berkeley, California 94720, USA

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ABSTRACT: High capacity and long cycle life are both desirable features for practical secondary cells. In this study, we compare two different synthesis processes for preparing active materials for lithium/sulfur cells using polysulfide and graphene oxide (GO) showing high sulfur utilization and cycling stability. The key factor determining cell performance is the oxygen-containing functional groups on GO and the fine structures. This study shows the possibility of application of GO for enhanced capacity and cycling stability.

1. Introduction:

The commercialization of lithium/sulfur cells has come closer to fruition recently. The benefits of lithium/sulfur cell technology are not only the high theoretical capacity but also the abundance of sulfur as a natural resource resulting low cost and low environmental impact. However, low sulfur utilization due to sulfur's insulating properties and capacity degradation resulting from dissolution-deposition and/or the polysulfide redox shuttle phenomenon are still not overcome in practical applications. [1] Material modification to mitigate these shortcomings of the lithium/sulfur cell are in high demand.

Composites of sulfur and graphene oxide (GO) have been investigated as promising candidates for the active material in lithium/sulfur cells since some composites have shown excellent cell performance. [2-17] GO is a unique carbon-based material because it has a variety of oxygen containing functional groups on the surface. It can be dispersed in aqueous solution easily which makes the synthesis of composites efficient and the resulting composites can be homogeneous. The behavior of the oxygen containing functional groups in various solutions is not fully understood and is still under study A recent report revealed that the functional groups on GO reacted with polysulfide just by mixing a GO suspension with a polysulfide solution, resulting in a composite of reduced GO and sulfur. [9] Also, the morphology of the material was influenced by the reaction rate of sulfur deposition depending on the conditions of the synthesis process [9] It has been

reported that sulfur deposition reactions are affected by the surface functional groups on graphene. [12] These studies suggest more possibilities of utilization of the GO's unique features for use in an active material for lithium/sulfur cells.

In this study, two different synthesis processes using GO and polysulfide to create different sulfur active materials are reported. The materials were characterized using scanning electron microscopy (SEM) and elemental analysis, i.e. CHNS analysis. These materials were evaluated in coin cells for rate capability and cycling stability.

2. Experimental Section:

Synthesis:

SGO-A: 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 commercial GO-water dispersion (4 mg/mL, Graphenea) was diluted with water to form 78 mL of suspension and sonicated for 1.5 hours. 82 mg CTAB (cetyltrimethylammoniumbromide) (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 and sonicated for 1.5 hours. The flake size of the original GO was 32.9 μm at D90, 16.6 μm at D50 and 6.63 μm at D10 from the information provided by the manufacturer of the GO. 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 1 hour. The mixture was slowly added to 50 mL of 2 M formic acid solution (Aldrich) and the mixture was stirred until the solution became clear from a milky colloid solution. Then the powder was filtered and washed with acetone and water, and dried at 45 °C in a vacuum oven for 12 hours. After drying, the sample was heated (heat treatment) in a tube furnace at 155 °C for 18 hours under Ar with a flow rate of 100 cc/min. An alumina boat containing the sample powders was wrapped with aluminum foil to prevent sulfur evaporation.

SGO-B: Na_2S_x solution and 81 ml of GO suspension were prepared according to the same method as for SGO-A. 50 mL of 2 M formic acid solution was added to the GO suspension and stirred. Then, the Na_2S_x solution was added drop-wise to the as-prepared GO suspension in formic acid and stirred for 6 hours. The mud-like solution containing the sulfur composite was centrifuged 3 times to replace the formic acid with distilled water.

SGO-B-G: GO suspension in formic acid and Na_2S_x solution were prepared according to the same process as described above. 82 mg CTAB (Sigma Aldrich) was added to the Na_2S_x solution drop-wise and stirred for 30 min. Then, the Na_2S_x solution with CTAB was added drop-wise to the as-prepared GO suspension in formic acid and stirred for 1 hour. Graphene nanomaterial (GN, carbon nano-flowers and multi-layer graphene flakes [21-22], provided by Jorma Jokiniemi) was added to the suspension of SGO-B-CTAB and stirred and sonicated. Then the powder was filtered and washed with acetone and

water, and dried at 45 °C in a vacuum oven for 12 hours. After drying, the sample was heated according to the same method as for SGO-A.

Material characterization:

SEM observation was conducted using a Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope. A secondary electron detector was used. An energy-dispersive X-ray spectroscopy (EDS) system was used for elemental x-ray analysis. The beam energy was 5 kV with 1 nm resolution.

Elemental analysis was performed using a Perkin Elmer 2400 CHNS/O series II analyzer. The combustion and reduction temperatures were 975 °C and 500 °C, respectively. The combustion parameters were 2, 10, 0, 0. The content of oxygen was estimated by the difference between 100% and the sum total of the contents of carbon, hydrogen, nitrogen and sulfur based on the assumption that there is no other element than carbon, hydrogen, nitrogen, sulfur and oxygen, considering the composition of the starting materials. The sodium in sodium sulfide should have been washed out when the powder samples were washed with water and acetone.

Thermogravimetric analysis (TGA) was conducted using a TA Instruments Q5000. A heating rate of 10 °C/min was used under the flow of N₂ with a flow rate of 100 cc/min.

Fourier transform infrared spectroscopy (FT-IR) was performed using a Perkin Elmer Spectrum One with an HATR assembly.

O K-edge X-ray absorption spectroscopy (XAS) was conducted at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL).

Electrochemical characterization:

The sulfur electrodes were fabricated by mixing the samples after the heat treatment, 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) 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. The sulfur content of the cathodes was 59% as a result of having 84% sulfur in the active materials and 70% active materials in the cathodes. The average sulfur loading of the electrodes was $\sim 0.8 \text{ mg/cm}^2$. 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 (1:2:2, by volume) was prepared. 50 μL of the electrolyte was used for evaluation of the electrochemical performance. 0.5 mol/kg LiNO_3 was used as an additive in the electrolyte.

Type CR2032 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 SGO-A or SGO-B-G 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) at the 0.2C rate (1 C = 1675 mA/g (sulfur)) for discharge and 0.1C rate for charge 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.

3. Results:

In order to create an intimate contact between sulfur and the carbon substrate, a sulfur deposition method was introduced in the synthesis process of the sulfur active material. The two synthesis processes, Procedure A and Procedure B are compared in Fig. 1 (a). Sodium polysulfide (Na_2S_x) as sulfur precursor and graphene oxide (GO) as the carbon substrate were used. Formic acid (HCOOH) was adopted to acidify the polysulfide to produce sulfur. These procedures are different regarding to the order of mixing the main three components, which are polysulfide, GO and formic acid. Procedure A included a mixing process of polysulfide and GO in advance of acidification of them by formic acid. In contrast to Procedure A, Procedure B was to mix GO and formic acid prior to acidification of the polysulfide. Although this seems to be a small difference, the resulting composites after the acidification were significantly different. The composites synthesized by Procedure A and Procedure B are labeled as SGO-A and SGO-B respectively.

The SEM image of SGO-A is shown in Fig. 2 (a). In the morphology of SGO-A, as has been reported in the previous studies, a flaky structure of the sulfur-GO composite was observed on the surface of the material. [2, 8, 9] The details of the sulfur deposition in Procedure A were studied in previous works. [9] It was found that the morphologies of the materials were strongly influenced by the sulfur deposition reaction rate. [9] When the SEM of SGO-A was zoomed out to see a wider area as shown in Fig. S1 (a), there were particles in the size range of 10 μm to 20 μm in random shapes. This morphology was created by both the slow sulfur deposition in the mixing process of polysulfide and GO and the fast sulfur deposition in the acidification step shown in Fig. 1 (a). [9] Slow deposition reactions induce sulfur nucleation by itself rather than deposition on the surface of GO, while a fast deposition reaction leads to a S deposit more on the surface of GO. [9] The shorter the mixing time of polysulfide and GO, the more sulfur deposition on the GO. [9] In Procedure B, the mixing process of polysulfide and GO was completely eliminated by mixing GO and formic acid in advance of adding polysulfide. Fig. 2 (b) shows the morphology of SGO-B. The composite was uniform fine particles in the size range of 0.5 μm to 2 μm without big chunks of sulfur particles, which is shown in the zoomed-out image, Fig. S1 (b) as well. Judging from the round shape of those particles of SGO-B in contrast to the flaky surface of SGO-A, sulfur covered the surface of GO almost completely.

An image illustrating the features of SGO-A and SGO-B is presented in Fig. 1(b).

The samples were analyzed by CHNS elemental analysis to check the contents of carbon, sulfur and oxygen. The contents of each element for GO, SGO-A and SGO-B are shown in Table 1.

The contents of each element were converted to the ratio vs. the content of carbon assuming the carbon in GO was stable enough so that the amount of carbon was not changed so much during the process. The ratios of sulfur and oxygen vs. carbon for GO, SGO-A and SGO-B are listed in Table S1 and compared in Fig. 3. In the original GO, the ratio of oxygen to carbon was 1.3 which corresponded to an oxygen content of 54%. These oxygen sources were from adsorbed water and functional groups containing oxygen on the surface of GO. [19, 20] The TGA result of GO also indicated corresponding weight loss of water and the functional groups as shown in Fig. S2. [20] The FT-IR spectrum of GO also showed the existence of carboxyl groups, epoxy groups and hydroxyl groups as shown in Fig. S3. Although the original GO contained a lot of oxygen, SGO-A did not contain any oxygen according to the results of the elemental analysis. This means that all of the oxygen was consumed during the synthesis. On the other hand, SGO-B maintained most of the oxygen even after the synthesis. In the previous study, it was found that oxygen was lost during the mixing process of polysulfide and GO. [9] Since there is no mixing step in Procedure B, the oxygen containing functional groups on GO remained during the synthesis. This means that the

acidification process did not consume the oxygen in the reactions. It is predictable that the oxygen functional groups remained because there was plenty of acid from formic acid in the solution so that the acidic functional groups on GO were not used in the sulfur deposition reaction. The maintenance of the oxygen functional groups during the sulfur deposition could support the homogeneous deposition of sulfur on the surface of GO due to the interactions between polysulfide and the oxygen functional groups. [12] The homogeneous deposition was also encouraged by the fast deposition reaction. [9] All polysulfide was converted to sulfur within 12 minutes as shown in the TGA results of SGO-B samples taken from the solution at different times in Fig. S4. The evaporation beginning at around 200 °C ending at 300 °C corresponded to evaporation of both sulfur and oxygen functional groups on GO. The sum of the contents of evaporated species was 90% which is consistent with the elemental analysis results, and the contents reached this number at 12 minutes after starting. When the sulfur deposition was fast, accessibility was dominant rather than stabilization so that sulfur deposition occurred on GO rather than creating separate sulfur particles. [9] Although other analytical methods, such as Raman spectroscopy [8], IR spectroscopy (Fig. S3) and X-ray absorption spectroscopy (Fig. S5), were used to check the remaining functional groups on GO in SGO-B, it was difficult to observe them because all the surfaces of GO were covered by sulfur.

Since the surface of SGO-B was covered by sulfur, addition of electronic conductivity to SGO-B was attempted. Graphene nanomaterial (GN) consisting of graphene nano-flowers and multi-layer graphene flakes was introduced to enhance the conductivity. [21, 22] CTAB was introduced to the polysulfide solution before acidification and GN was introduced at the end of the synthesis. Although CTAB is a known surfactant, it was revealed that CTAB works also as a precursor of a layer on the material which enhances the cell performance. [8] The layer is created by the reactions of CTAB with polysulfide and sulfur during the heat treatment. [8] This is the reason why CTAB was introduced to the polysulfide solution. The modified SGO-B with GN is labeled as SGO-B-G. A SEM image of SGO-B-G before adding GN is shown in Fig. 2 (c) and of SGO-B-G is shown in Fig. 2 (d). The size of multi-layer graphene flakes and graphene nano-flowers in GN is about 50 nm. [21, 22] It can be observed that the particles of sulfur-GO composite were surrounded by GN. To check the distribution of sulfur and carbon, EDS mapping was conducted for SGO-B-G as shown in Fig. S7. It was verified that sulfur and carbon were homogeneously distributed on the particles. CTAB as the surfactant helped graphene additives to be dispersed so that it provided a sufficient conductive network.

SGO-A and SGO-B-G were heat-treated at 155 °C for 18 hours. Although this type of heat treatment for sulfur containing materials is considered in general to distribute sulfur on matrices by melting sulfur once, the heat treatment for the SGO composites was performed to obtain a layer created

by the reactions between CTAB and sulfur and polysulfides during the heat treatment. [8] It was confirmed that the morphologies of the SGO composites were mostly determined in the sulfur deposition step and there were not big changes in the morphologies before and after the heat treatment (Fig. S8).

The electrochemical performance of SGO-A and SGO-B-G after the heat treatment was examined. The results of rate capability tests and the following cycling performance are shown in Fig 4 (a). SGO-A showed higher initial capacity and better rate capability than SGO-B-G. Especially, the difference in the initial capacity was significant in which SGO-A showed 1500 mAh/g while SGO-B-G showed 1100 mAh/g. However, when the cycling test was continued over 100 cycles, SGO-B-G showed better cycling stability than SGO-A as shown in Fig. 4 (b). The voltage profiles of the second cycle, 90th cycle and 200th cycle for SGO-A and SGO-B-G are shown in Fig. 4 (c). The typical voltage profile of sulfur reduction which consisted of two plateaus was obtained. The overvoltage for SGO-A and SGO-B-G were almost same while the capacity for SGO-A was higher than SGO-B-G at the second cycle. This can be explained from the observation of the morphology and the results of elemental analysis. SGO-A has a more flaky shape than SGO-B which means GO is more on the surface than SGO-B. Elemental analysis showed zero oxygen content in SGO-A as shown in Fig. 3 and Table 1 and S1, which indicates that GO was converted to reduced GO, i.e. graphene with some defects, during the mixing process. Reduced GO is known to be more electron conductive than original GO. [14-16] As the results show, SGO-A has

conductive reduced GO on the surface. This morphology enables the material to exhibit high sulfur utilization at the beginning. On the other hand, SGO-B has a morphology which has more sulfur on the surface. Although SGO-B-G has a more complicated morphology than SGO-B because it has CTAB and GN, it is supposed to have more sulfur on the surface than SGO-A like as SGO-B. Furthermore, SGO-B retained some oxygen as shown by elemental analysis, that means GO retains the oxygen functional groups. SGO-B-G showed similar overvoltage to that of SGO-A thanks to the additional GN though, the initial sulfur utilization was limited by those features. These can be also the reason for the better rate capability of SGO-A than SGO-B-G. However, when the voltage profiles in 90th cycle and 200th cycle are compared, while these are almost exactly same for SGO-B-G, the 200th profile has more overvoltage and less capacity than the 90th cycle for SGO-A as shown in Fig. 4 (c). Although the overvoltage for SGO-B-G is higher than SGO-A, it remains at the same level between cycle 90 and cycle 200. The good retention of the capacity for SGO-B-G can be attributed to the maintenance of the oxygen containing functional groups on GO as seen in the result of elemental analysis. This result suggests that the oxygen containing functional groups on GO may sacrifice electron conductivity though, they can work to keep sulfur in the conductive matrix resulting high cycling stability.

In order to examine the effect of the fine composite particles and immobilization by GO on the cell performance, SEM images of the sulfur

electrode composed of SGO-A and SGO-B-G before and after cycling were obtained. Fig. 5 (a) and (b) show the fresh electrode composed of SGO-A and SGO-B-G respectively. Corresponding to the original morphologies of SGO-A and SGO-B-G, particles in the size range of 10 μm to 20 μm surrounded by smaller particles of carbon additives are seen in the electrode of SGO-A, while particles in the size range of 0.5 μm to 2 μm are connected each other with the carbon additives for the electrode of SGO-B-G. Fig. 5 (c) and (d) show the 15 times cycled and charged electrode of SGO-A and SGO-B-G respectively. In the cycled electrode of SGO-A in Fig. 5 (c), it can be observed that big sulfur plates in the size of about 10 μm emerge among the composite. It is the consequence of that once dissolved and reduced sulfur as polysulfides and converted to lithium sulfide deposited out of the composite when it was oxidized during the charge process. Once big sulfur plates are created, it is hard for all of them to get involved in the electrochemical reactions again because of lack of conductivity. In contrast to SGO-A electrode, the cycled electrode of SGO-B-G in Fig. 5 (d) shows no big plates of sulfur and well maintained original fine morphology. The same set of images as Fig. 5 in low magnification are presented in Fig. S11. This observation supports the idea that good cycling stability in the cell using SGO-B-G was achieved due to the immobilization by GO functional groups in the fine uniform structure rather than the big particles of SGO-A.

This study showed the possibility of application of GO for capacity increase and cycling stability depending on the protocol in the synthesis process.

Although the final aim is to obtain cycling stability with high capacity, understanding how the materials can be modified for different purposes gives important knowledge for future applications.

5. Conclusions:

Two different synthesis processes of active materials for lithium/sulfur cells using polysulfide and graphene oxide (GO) showed different cell performances. By mixing the GO and acid solution prior to adding polysulfide, the homogeneous deposition of sulfur onto GO was achieved due to the rapid sulfur deposition reactions and the interaction between polysulfide and the oxygen-containing surface functional groups on GO. The active material based on this method showed higher cycling stability thanks to the interaction between sulfur and the well-maintained oxygen-containing functional groups on GO.

ASSOCIATED CONTENT

AUTHOR INFORMATION

Corresponding Author

* Elton J. Cairns

Energy Storage and Distributed Resources Division, Lawrence Berkeley
National Laboratory, and Department of Chemical and Biomolecular
Engineering, University of California, Berkeley

ejcairns@lbl.gov

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Table 1. The contents of carbon, hydrogen, nitrogen, sulfur and oxygen in GO, SGO-A and SGO-B determined by CHNS elemental analysis.

Element	GO	SGO-A	SGO-B
C	39.78	15.45	10.43
H	2.73	1.63	0.41

N	0.11	0.42	0
S	4.02	82.51	79.52
O	53.36	0	9.64

Fig. 1 (a) Diagram of the preparation of the sulfur/GO composites comparing two procedure, Procedure A and Procedure B. (b) The graphical images illustrating the features in the morphologies of SGO-A and SGO-B.

Fig. 2 SEM images of SGO-A prepared by Procedure A (a), SGO-B prepared by Procedure B (b), SGO-B-G before adding GN (c) and SGO-B-G (d).

Fig. 3 The ratios of sulfur and oxygen vs. carbon in GO, SGO-A and SGO-B to compare the amount change of sulfur and oxygen during the synthesis.

Fig. 4. (a) The rate capability tests and the following cycling performances of SGO-A and SGO-B-G. (b) The cycling performance until 300 cycles. (c) The voltage profiles of 2nd, 90th and 200th cycles for SGO-A and SGO-B-G.

Fig. 5 SEM images of electrodes composed of SGO-A before cycling (a) and after 15 cycles (b) and electrodes composed of SGO-B-G before cycling (c) and after 15 cycles (d) magnified 5,000 times.