High Performance Pure Sulfur Honeycomb-like Architectures Synthesized by Cooperative Self-assembly Strategy for the Lithium/Sulfur Battery

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Electronic Supplementary Information (ESI)
1. Experimental details:

Materials:

Sodium thiosulphate (Na$_2$S$_2$O$_3$), oxalic acid (H$_2$C$_2$O$_4$), sulfur (S), and SDBS were all purchased from Sigma Aldrich (Australia). All the chemicals were used as received without any further purification.

Preparation of honeycomb-like sulfur:

Firstly, 3.60 g H$_2$C$_2$O$_4$ was dissolved in 250 mL distilled water at room temperature under vigorous stirring. Subsequently, 3.16 g Na$_2$S$_2$O$_3$ was also dissolved in 250 mL distilled water, and then 0.21 g SDBS was added and stirred vigorously. Afterwards, the H$_2$C$_2$O$_4$ solution was dropped into the Na$_2$S$_2$O$_3$ and SDBS solution within 20 minutes. After that, 30 minutes were allowed for the completion of the reaction under vigorous stirring. Then, over 500 mL distilled water was added into the solution. A light yellow powder was obtained after centrifuging. The light yellow powder was then dried in a vacuum oven at 45 °C for 24 hours after washing several times with distilled water and acetone. For comparison, sulfur particles without pores were prepared following a similar procedure in the absence of SDBS.

Physical Characterization:

The structure of the sulfur particles was characterized by X-ray diffraction (XRD) using a GBC MMA X-ray generator and diffractometer with Cu Kα radiation (λ = 1.5418 Å), employing a scanning rate of 5°/min in the 2θ range from 10° to 70°. The morphology of the sulfur powder was investigated by field emission scanning electron microscope (FE-SEM; JEOL JSM-7500FA). The specific surface area of the powders was examined by gas sorption analysis using the Brunauer-Emmett-Teller method (Quanta Chrome Nova 1000).

Electrochemical measurements:

The working electrodes were prepared by mixing 50 wt. % as-synthesized sulfur powder with 40 wt. % carbon black and 10 wt. % polyvinylidene fluoride (PVDF) binder in
N-methyl-2-pyrrolidinone (NMP) solvent. The well-mixed slurry was tape-cast onto a sheet of aluminium foil substrates. The commercial sulfur was treated in the same way for comparison. The coated electrodes were dried in a vacuum oven at 45 °C for 48 h and then pressed. Subsequently, the electrodes were cut to a 1 × 1 cm² size. The loading weight of the active material is around 1 mg/cm². 1 M lithium bistrifluoromethanesulfonamide (LiTFSI) in poly (ethylene glycol) dimethyl ether 500 (PEGDME 500) was used as electrolyte. 0.1 M LiNO₃ salt was used as an electrolyte additive. To compare the effect of the electrolyte, another electrolyte was also prepared, which is 1 mol/L lithium bistrifluoromethanesulfonamide (LiTFSI) in 1,3-Dioxolane(DOL) / 1,2-Dimethoxyethane (DME) (1 : 1 by volume) with 0.1 mol L⁻¹ LiNO₃ as an additive. CR2032 coin cells were assembled in an Ar-filled glove box. Charge-discharge testing was carried out with a LAND battery test system at a current density of 50 mA g⁻¹ with a voltage range of 1.5–3.0 V. Cyclic voltammetry (CV) and AC impedance measurements were performed using a Biologic VMP-3 Multichannel electrochemistry workstation at a scanning rate of 0.1 mV s⁻¹ and a frequency range of 1 00 KHz - 0.01 Hz, respectively.
2. Supplemental Table and Figures

**Figure S1. Details of the synthesis.**

Figure S1 shows the details of the synthesis. Solution A is 250 mL aqueous solution with 2.4 mM SDBS and 10 mM Na$_2$S$_2$O$_3$, while solution B is 250 mL distilled water with 40 mM H$_2$C$_2$O$_4$. In solution A, the concentration of SDBS is much higher than 1.2 mM, and the concentration of salt (Na$_2$S$_2$O$_3$) is also quite high, thus the SDBS prefers to form lamellar micelles. After dropping solution B into solution A, solution C was produced, which is 500 mL distilled water with 1.2 mM SDBS and 5 mM Na$_2$S$_2$O$_3$. As both the concentrations of SDBS and salt decrease, the SDBS lamellar micelles were transformed to spherical micelles which will form when the concentration of SDBS is equal or only a little bit higher than 1.2 mM and the concentration of salt (Na$_2$S$_2$O$_3$) is low. At the same time, the sulfur starts to precipitate. Thus, cooperative self-assembly occurs between the sulfur and the SDBS spherical micelles. Then, many more sulfur particles are produced, resulting in further condensation. Secondly, after adding a large amount of H$_2$O into solution C, the SDBS spherical micelles break because of the low concentration of SDBS and salt, and then the SDBS is removed. Finally, the sulfur particles with porous honeycomb-like structure are
obtained.

Table S1 Parameters of the comparative experiments.

<table>
<thead>
<tr>
<th>Conditions (Figures in Fig.S2)</th>
<th>Starting concentration of SDBS in solution A</th>
<th>Final concentration of SDBS in solution C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Fig. S2a)</td>
<td>4.8 mM</td>
<td>2.4 mM</td>
</tr>
<tr>
<td>2 (Fig. S2b)</td>
<td>2.4 mM</td>
<td>1.2 mM</td>
</tr>
<tr>
<td>3 (Fig. S2c)</td>
<td>1.2 mM</td>
<td>0.6 mM</td>
</tr>
<tr>
<td>4 (Fig. S2d)</td>
<td>0.6 mM</td>
<td>0.3 mM</td>
</tr>
</tbody>
</table>

The comparative experiments with different starting concentrations of SDBS were carried out. As shown in table S1, there are four different starting concentrations of SDBS were applied, 4.8 mM, 2.4 mM, 1.2 mM and 0.6 mM respectively. After adding 250 mL 40 mM $\text{H}_2\text{C}_2\text{O}_4$ solution (solution B) into solution A, the concentrations of SDBS in solution C have reduced to 2.4 mM, 1.2 mM, 0.6 mM, 0.3 mM respectively.
**Figure S2. FESEM images of the as-prepared sulfur with different starting concentrations of SDBS: (a) 4.8 mM, (b) 2.4 mM, (c) 1.2 mM, (d) 0.6 mM.**

Fig. S2 presents the relative FESEM images of the obtained sulfur particles in the comparison experiments. It is shown in Fig. S2a that there is not any porous structure of the sulfur particles can be observed when the start concentration of the SDBS is 4.8 mM. Because after adding solution B into solution A, the concentration of SDBS reduced to 2.4 mM, thus during all the reaction, the concentration of SDBS is much higher than 1.2 mM, which is the critical micelle concentration of SDBS to form spherical micelles. The second condition was using 2.4 mM as the starting concentration of SDBS, after dropping solution B into solution A, the concentration of SDBS decreased to 1.2 mM, and has been kept for 30 mins. Thus, the cooperative self-assembly occurs between the sulfur and the SDBS spherical micelles. Fig S2b shows that honeycomb-like porous sulfur was obtained. In condition 3, the starting concentration of SDBS is 1.2 mM, so in solution A SDBS exists as spherical micelles, thus, a little amount precipitated sulfur can cooperative self-assemble with the
spherical SDBS micelles at the very beginning of the reaction after adding solution B. That’s why there some pores have been observed in Fig.S2c. In the fourth condition, 0.6mM was used as the starting concentration of SDBS, after the reaction, the final concentration of SDBS is only 0.3 mM, the concentration of SDBS is much lower than the critical micelle concentration of SDBS(1.2 mM). thus there is no spherical micelles exist during all the reaction progress, therefore the FESEM images of the obtained sulfur in Fig S2d shows no pores either. Based on the discussion above, it was found that the optimum starting concentration of SDBS was 2.4 mM.
Figure S3. The charge/discharge profiles of the selected cycles of the honeycomb-like cathode.

The charge-discharge profiles in Fig. S4 are assigned to the two-step reaction of sulfur with lithium, a typical process in Li/S batteries. The charge and discharge potential values of the upper and lower plateaus are stabilized at approximately 2.5 and 2.27 V, and 2.44 and 1.97 V, respectively.
A comparison of the rate capability between the honeycomb-like sulfur electrode and the commercial sulfur electrode is shown in Fig. S4. The discharge capacity of the honeycomb-like sulfur electrode decreases gradually as the current density is increased from 50 to 1600 mA g\(^{-1}\), and then it recovers most of its original capacity when the current density is reduced back to 50 mA g\(^{-1}\). After 25 cycles, its discharge capability can still reach 900 mAh g\(^{-1}\). In contrast, the rate capability of the commercial sulfur electrode is very bad. When the current density rises to 1600 mA g\(^{-1}\), the retained discharge capacity of the commercial sulfur electrode is only about 20 mAh g\(^{-1}\).
It is well known that compare to PEGDME 500 solvent, 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) have good ionic conductivity and low viscosity which is essential to enhance the high rate capabilities[1, 2]. Thereby, in order to optimize the high rate behaviour of the honeycomb-like sulfur cathode, 1 mol/L lithium bistrifluoromethanesulfonamide (LiTFSI) in a mixed solvent of 1,3-Dioxolane(DOL) / 1,2-Dimethoxyethane (DME) (1 : 1 by volume) with 0.1 mol L$^{-1}$ LiNO$_3$ as an additive was used as electrolyte to test the rate capabilities of the honeycomb-like sulfur cathode as well. As shown in Figure S5, when the current densities are lower than 400 mA g$^{-1}$, the honeycomb-like sulfur cathode in the electrolyte with a mixed solvent of 1,3-Dioxolane(DOL)/1,2-Dimethoxyethane (DME) (1 : 1 by volume) shows lower capacities than in the electrolyte with solvent of PEGDME due to high solubility of polysulfides in DOL/DME. But when current densities are higher than 400 mA g$^{-1}$, the honeycomb-like sulfur cathode in the electrolyte with a mixed solvent of 1,3-Dioxolane(DOL)/1,2-Dimethoxyethane (DME) (1 : 1 by volume) presents much higher capacities than in the electrolyte with solvent of PEGDME. In addition, when the current density is increasing, the improvement becomes much obvious. Specifically, the capacities has been improved 140mAh g$^{-1}$ at 800 mA g$^{-1}$ and 250 mAh g$^{-1}$ at 1600 mA g$^{-1}$. It further confirmed that the high-rate performance depends on the ion diffusion speed and the electronic conductivity of the electrolyte solvent.