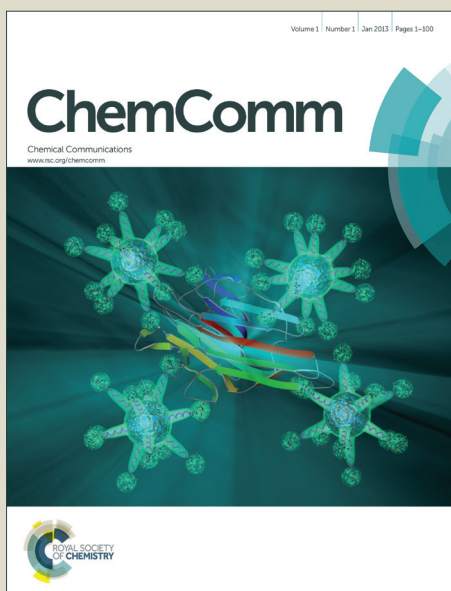


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## COMMUNICATION

## High Sulfur Loading and High Capacity per Area Lithium Sulfur Cathode: Binder-free Carbon Fibers Cloth/sulfur Material

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**A high capacity per area (>7 mAh cm<sup>-2</sup>) sulfur cathode with high sulfur loading (6.7 mg cm<sup>-2</sup>) was fabricated by synthesizing a carbon fiber cloth sulfur composite via a simple method. It is worth noting that an ingenuity method is adopted which can improve performance of Li-S battery by forming *in-situ* polysulfide ions.**

Lithium sulfur battery (Li-S) is regarded as one of the most promising systems for next generation batteries due to a high theoretical capacity of 1675 mAh g<sup>-1</sup> and a higher specific energy of 2600 Wh kg<sup>-1</sup>. Additionally, in comparison to conventional cathode materials, elemental sulfur is an abundant resource, low cost and environmentally friendlier.<sup>1-4</sup> Despite these advantages, Li-S systems still are plagued with several drawbacks. The major one is the diffusion of polysulfide ions (Li<sub>2</sub>S<sub>n</sub>, 2 < n ≤ 8), the reduction products of sulfur, diffusing into electrolyte during charge and discharge cycling. The long chains soluble polysulfide ions can diffuse to anode side, where they are reduced to short chains polysulfide ions, and those short chains polysulfide ions diffuse back to the positive electrode and then are reoxidized into long chains polysulfide ions.<sup>2,5</sup> In addition, the poor electrical conductivity of elemental sulfur and insoluble Li<sub>2</sub>S or Li<sub>2</sub>S<sub>2</sub> causing only low utilization of the active material, moreover, some polysulfide ions can be fully reduced on the anode surface, leading to loss of the active sulfur.<sup>1,5</sup> These problems will cause the significant capacity fading, low Coulombic efficiency and insufficient cycle life.

During the last few years the electrochemical properties of the Li-S system have been greatly improved. Having only 50 cycles with low and unstable capacities at the beginning, the barrier of 1000~1500 relatively stable cycles with high capacities around 600~1000 mAhg<sup>-1</sup> sulfur have been reached in recent publications.<sup>6-9</sup> Commercial applications have been completely satisfied with such a long cycle life; Additionally the very high cycle stabilities at very high currents (5~40C, 1C=1.6A g<sup>-1</sup>) with good capacities have been reported.<sup>11</sup>

Although many materials exhibited very good cycling stability as well as good rate capability, it is noticed that a major problem of "two lows" was ignored in many publications reports when meeting the demand for high capacity energy storage systems. The "two lows" means the low sulfur content in the composite slurry and low

sulfur loading in the cathode.<sup>2-4</sup> In general, the lower sulfur content and sulfur loading, the higher the specific capacity due to the specific capacities were calculated based on the S mass only, especially low sulfur loading on electrodes was easier to get better performance of batteries. So many studies have focused on cells exhibiting extremely high capacity per gram of sulfur and efficient performance. Some superior results that reported recently are summarized as listed in Table S1 (see ESI<sup>†</sup>). It is found that most results are derived from cathodes with sulfur loading of less than 2 mg cm<sup>-2</sup>. It should be noted that the very low sulfur loading leads to the very low surface capacities which is below 3 mAh cm<sup>-2</sup> electrode (bold in Table S1), which is even lower than the capacity per area of commercial lithium ion batteries (LIB).<sup>4</sup> Li-S may be not as good as commercial LIB, because the low sulfur loading on electrode will greatly offset the advantage of the high energy density of Li-S battery.

Moreover, On one hand some materials have low sulfur content in the composite slurry or on electrode (<60% S) because of addition of conductive carbon and binders, on the other hand some materials contain more than 80% sulfur content, but the electrode coating (<30μm, see Table S1) is much thinner than commercial LIB (>100 μm). In general, it is not a good way to improve specific capacity of cathode by reducing the thickness of the coating on electrode. To achieve higher specific energy, high surface capacity of cathodes is required, which means high sulfur loading and utilization of sulfur are essential. Despite it is a challenge to improve the utilization of sulfur and the sulfur loadings simultaneously, it needs to be overcome to take advantage of the high energy density of Li-S batteries for the future commercial applications.

In this paper, a high capacity per area (>7 mAh cm<sup>-2</sup>) sulfur cathode with high sulfur loading (6.7 mg cm<sup>-2</sup>) was fabricated by synthesizing a carbon fiber cloth sulfur (CFC/S) composite via a simple method. The cycling performances of cell with the CFC/S composite as cathode material were tested. Approximately 6.7 mg cm<sup>-2</sup> sulfur loading of the CFC/S material cathode was able to retain a specific capacity of 1100 mAh g<sup>-1</sup> after 50 cycles at 0.3 mA cm<sup>-2</sup> between 1.5 V and 2.8 V. High reversible capacity per area (>7 mAh cm<sup>-2</sup>) and a retention rate of 96% was observed during 50 cycles of

charge-discharge process. To the best of our knowledge, it is the highest value among the results of previous reports (see Table S1).

The synthesis of the CFC/S composite is described in Fig. S1 (see ESI†). For further investigation, the morphology and microstructure of the CFC and CFC/S composites materials were observed by SEM. It shows the general morphology for the carbon fiber cloth in Fig. 1 a, b, c. The original cloth used in this work is actually an artificial pseudo-2D network of cotton threads in compact bundles through simple weaving (Fig. 1a, b). Each bundle comprises many strips with an average diameter of 7 $\mu$ m, and whole carbon fibers were densely woven into conductive network after carbonization. Close contact with each other of the carbon fibers leads to the higher overall conductivity than the traditional spherical carbon/sulfur composite. To confirm the presence of sulfur and carbon, energy-dispersive X-ray spectroscopy (EDS) mappings were performed. As shown in Fig. 1 d1, d2, e1, e2, f1, f2, the maps indicate a complete and homogeneous infiltration of sulfur in the CFC network. Red and yellow dots respectively correspond to the carbon and sulfur elemental map of CFC/S, no bulk sulfur particles were found.

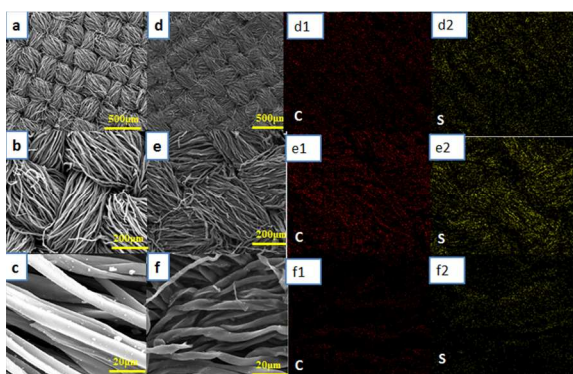


Fig. 1 SEM images of the CFC a, b, c and CFC/S d, e, f; EDX mapping of the CFC/S (d1, d2, e1, e2, f1, f2) reveals the highly dispersed state of sulfur (yellow) on CFC (carbon, red)

Moreover, the cross-section of CFC/S was observed by SEM and EDS as shown in Fig. 2. Most of carbon fibers are hollow fibers and sulfur was diffused into the inside and outside of the carbon fiber (as shown in Fig. 3D1), so it can load more sulfur than other solid carbon fiber cloth of reported.<sup>12,13</sup> The thickness of CFC/S cathode was about 150 $\mu$ m. The longer size and densely woven carbon fibers may be beneficial to reduce the contact resistance between the fibers and to improve the conductivity of the electrode. Therefore, the CFC/S can still maintain the good electrical conductivity, even at high sulfur loading; moreover, long bundles fibers can play a positive role in expanding of sulfur during discharge when loading more sulfur. The good electrical conductivity of 1.58 S cm<sup>-1</sup> was determined using the four-probe technique on a CFC disk. After the infiltration of sulfur into the CFC, the electrical conductivity of the CFC/S composite (containing sulfur 6.7 mg cm<sup>-2</sup>) was reduced to 0.37 S cm<sup>-1</sup>; it can be ascribed to the surfaces of the carbon fibers were covered by elemental sulfur.

The discharge-charge profiles of the CFC/S which the sulfur loading respectively was about 3.8, 5.3, 6.7, 8.0 mg cm<sup>-2</sup> as shown in Fig. 3. The amount of electrolyte is 200  $\mu$ L of every button battery. Obviously, when the sulfur loading is 3.8 mg cm<sup>-2</sup>, the profile of battery is typical discharge-charge profiles of the carbon/sulfur composite<sup>3-6</sup>. The discharge capacity is very high at the first cycle, and then rapidly decreases during initial several cycles. This result can be attributed to some reduction product (polysulfide intermediates) of sulfur dissolving into electrolyte of the on

electrode. The problem of sulfur dissolving into electrolyte will cause the significant capacity fading. The amount of polysulfide ions in electrolyte would be increase in discharge-charge process, finally, the concentration of dissolved polysulfide ions was quasi-dynamically balance.<sup>6</sup> The cyclic stability and rate capability of the Li-S battery will be improved when the existence of dissolved polysulfide ions in electrolyte.<sup>6,13-17</sup> The certain amount polysulfide concentration during discharge/charge process not only facilitated the transfer of polysulfide to the electrode/electrolyte interface and the utilization of sulfur, but also alleviated polarization of reversible polysulfide reduction/oxidation.<sup>6,13-17</sup> Adding polysulfide ions in electrolyte can be considered beneficial to deliver a stable capacity of the battery during cycle.<sup>13-17</sup>

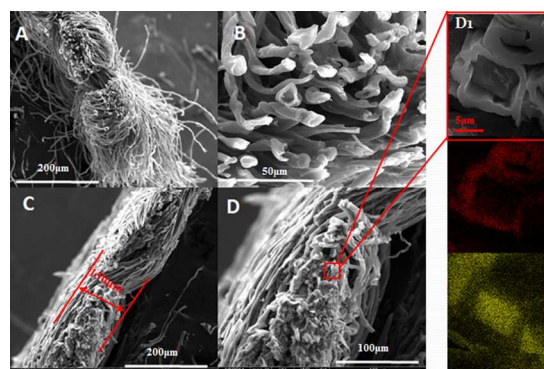


Fig. 2 SEM images (A, B, C, D) and EDX mapping of the cross-section of CFC/S (sulfur is yellow, carbon is red), sulfur loading 6.7 mg/cm<sup>2</sup>

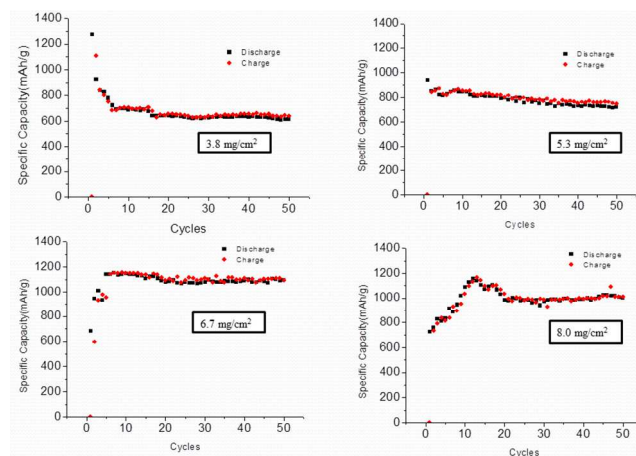


Fig. 3 Charge-discharge performance of the CFC/S electrode at different sulfur loading in the potential rang of 1.5~2.8V, 0.3 mA cm<sup>-2</sup> current density.

The processes which the concentration of dissolved polysulfide ions reached a quasi-dynamically balance have quickly finished when the sulfur loading increases to 5.3 mg cm<sup>-2</sup>, the capacity fading appeared only in the first cycle. With the increasing of sulfur loading and the corresponding amount of electrolyte, the concentration of dissolved polysulfide ions may be easier to reach a quasi-dynamically balance. And then, the ratio of polysulfide ions diffusion into the anode becomes smaller, the more active material is restricted in cathode area so that the stability of the cathode can be maintained. When the amount of sulfur increases to 6.7 mg cm<sup>-2</sup> even 8.0 mg cm<sup>-2</sup> on electrode, a significant feature of the low capacity of battery in the initial cycles was observed. As shown in Fig. 3, when sulfur loading on electrode was 6.7 mg cm<sup>-2</sup>, the

discharge specific capacity of the CFC/S composite cathode is only 687.3 mAh g<sup>-1</sup> (based on the mass of sulfur) at the first cycle. However, it reaches the highest capacity of 1156.0 mAh g<sup>-1</sup> in the 8th cycle. Finally, the CFC/S composite cathode retains a reversible capacity of 1100.4 mAh g<sup>-1</sup> after 50 cycles with a retention rate of 96%. Moreover, Fig. S2 shows the typical charge-discharge profiles of Li-S cell in 1<sup>st</sup>, 2<sup>nd</sup>, 8<sup>th</sup>, 50<sup>th</sup> cycle. Two voltage plateaus appeared at around 2.3 V and 2.0 V in the discharge curves. We suppose that not all sulfur takes part in the reaction with lithium ion because of poor conductivity when high sulfur loading in the initial several cycles, step by step some of polysulfide ions dissolving into the electrolyte, more and more sulfur participating in the discharge reaction. The polysulfide ions formed *in-situ* on electrode diffused into electrolyte and improved the performance of Li-S battery when the concentration of dissolved polysulfide ions reached a quasi-dynamically balance. The result of stable cycles is consistent to result in literatures by adding polysulfide ions into electrolyte.<sup>13-17</sup> Moreover, when increasing the electrolyte amount to 400 μL, even electrode with 7 mg cm<sup>-2</sup> sulfur loading, the capacity has visibly declined at initial cycles, despite a process of slow capacity fading in the last several cycles (Fig. S3). Therefore, how to well fit the loading of sulfur and electrolyte amount to retard the further dissolution of polysulfide and improve the performance of the Li-S battery is the key.<sup>6</sup> However, this method that the polysulfide ions formed *in-situ* on electrode diffusing into the electrolyte is a simple and low cost way to improve the performance of Li-S battery.

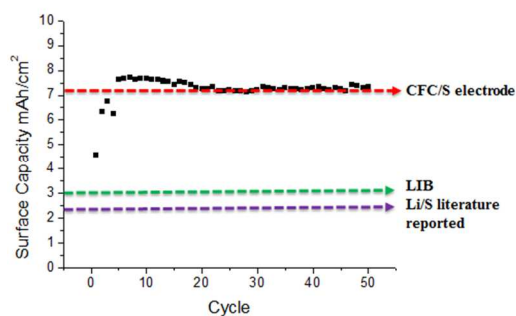


Fig.4 Comparison of capacity per area of CFC/S electrode with selected literature reports (purple dotted line) and LIB (green dotted line)

As shown in Fig 4, a high capacity per area (>7 mAh cm<sup>-2</sup>) of sulfur cathode with high sulfur loading (6.7 mg cm<sup>-2</sup>) was compared with lithium ion battery (LIB) and other carbon/sulfur composites with selected literature reports (see Table S1). It is clearly that the value of 7 mAh cm<sup>-2</sup> cathode was 2~3 times higher than the values of LIB and various carbon/sulfur composites reported in literatures. The capacity per area of LIB is usually about 3.0 mAh cm<sup>-2</sup>.<sup>4</sup> The capacity per area of carbon/sulfur composites reported in literatures are less than 3 mAh cm<sup>-2</sup> (bold words in Table S1). It should be noted that the very low sulfur loading (0.4~2.0 mg cm<sup>-2</sup>) leads to the very low surface capacities. Li-S battery may be not as good as conventional LIB because of the low sulfur loading on electrode which will greatly offset the advantage of the high energy density of Li-S battery. To achieve higher specific energy, high capacity per area of cathodes needs to be achieved to take advantage of the high energy density of Li-S batteries for the future commercial applications.

## Conclusions

In summary, a high capacity per area (>7 mAh cm<sup>-2</sup>) sulfur cathode with high sulfur loading (6.7 mg cm<sup>-2</sup>) was prepared by

synthesizing a carbon fiber cloth sulfur composite via a simple method. High sulfur loading and high capacity per area of CFC/S composite cathode is beneficial to achieve the really high specific energy of lithium sulfur batteries. More importantly, an ingenuity method is adopted which can suppress the polysulfide further dissolution and improve performance of Li-S battery by forming *in-situ* polysulfide ions on electrode with a highly sulfur loading. The CFC/S composite cathode retains a reversible capacity of 1100.4 mAh g<sup>-1</sup> after 50 cycles with a retention rate of 96%. Moreover, the low-cost CFC/S composite can be easily produced on a large scale, so it is a promising candidate for really commercial application high specific energy Li-S batteries.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Materials synthesis and cell assembly. See DOI: 10.1039/c000000x/

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