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## COMMUNICATION

## Elastic porous carbon material supported sulfur cathode for Li-S batteries design

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In this work, we present a three-dimensional elastic carbon foam as a current collector and freestanding electrode for Li-S batteries. Sulfur content of approximately 43.93% which was based on the all weight of cathode was achieved. The non-additive S cathode with good elasticity shows a first discharge specific capacity of 893 mA h g<sup>-1</sup> and a specific capacity of 544 mA h g<sup>-1</sup> after 30 cycles at moderate rates. A coulombic efficiency of 98% over 100 cycles is achieved.

In recent years, new electric vehicles have attracted increasing attention because of the urgent need for energy conservation and the improvement of environmental awareness. Therefore, efficient energy storage has become a top priority.<sup>[1-3]</sup> Among the various types of rechargeable batteries, the lithium-sulfur (Li-S) battery shows great promise because of its high theoretical specific capacity (1,675 mA h g<sup>-1</sup>) and energy density (2,600 W h kg<sup>-1</sup>).<sup>[4, 5]</sup> In addition, sulfur is abundant on earth, easily available, and environmentally friendly. However, the practical application of Li-S batteries has encountered a series of obstacles, such as low active material utilization and poor cycle life.<sup>[3, 4, 6]</sup> In fact, the low electrical conductivity of sulfur (5 × 10<sup>-30</sup> S cm<sup>-1</sup> at 25 °C), the solubility of intermediate lithium polysulfide (Li<sub>2</sub>S<sub>n</sub>, n > 2), and the large volume change (up to 80%) mainly lead to the low utilization of active materials and poor coulombic efficiency.<sup>[7, 8]</sup> One of the most important strategies in solving the aforementioned issues is to effectively combine sulfur with electron conductive additives.<sup>[9]</sup> In recent years, various efforts have been devoted to the development of Li-S batteries by encapsulating or mixing sulfur with conducting materials, including carbon black,<sup>[10, 11]</sup> porous carbon,<sup>[12, 13]</sup> hollow carbon spheres,<sup>[14, 15]</sup> cnts<sup>[16, 17]</sup>, graphene(oxide)<sup>[18, 19]</sup> and conducting polymer<sup>[8, 20]</sup>. Other novel approaches include the application of nanoscale

sulfur<sup>[21, 22]</sup> and Li<sub>2</sub>S particle<sup>[23-25]</sup> as active materials. Meanwhile, the efforts toward interlayers have achieved significantly positive results.<sup>[26-28]</sup>

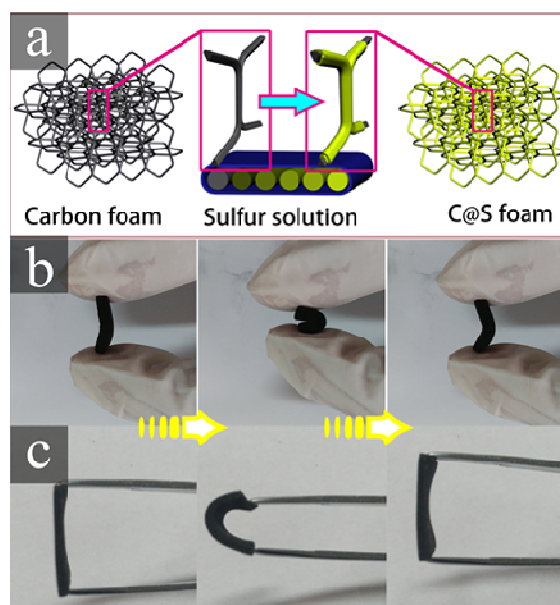


Fig. 1 (a) Schematic illustration of the fabrication of C@S foam cathode, the digital photos of flexible elasticity of (b) the C foam and (c) C@S foam.

The portable, flexible and wearable electronics that have emerged in recent years depend largely on flexible battery materials.<sup>[7, 29, 30]</sup> Thus, extensive efforts have been devoted to the fabrication of flexible materials for energy storage.<sup>[7, 29, 31-33]</sup>

To address the need for flexible batteries, we choose a novel elastic carbon material to construct battery cathode. To our best knowledge, the three dimensional flexible carbon foam is the first time used into lithium sulfur battery. Specifically, we propose a three-dimensional carbon foam material as a freestanding electrode without binder. Meanwhile, the carbon foam with a low density less than 10 mg cm<sup>-3</sup> is more lightweight than other carbon materials. So it owns a high

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potential to enhance the energy density. Meanwhile, the carbon foam as a whole part for sulfur carrier could facilitate the electron transfer. Furthermore, the porous carbon foam with excellent elasticity has inherent advantages to structure flexible batteries. So the commercial melamine foam-derived carbon foam has great potential in the field of industrial fabrication of lithium sulfur batteries large scale.

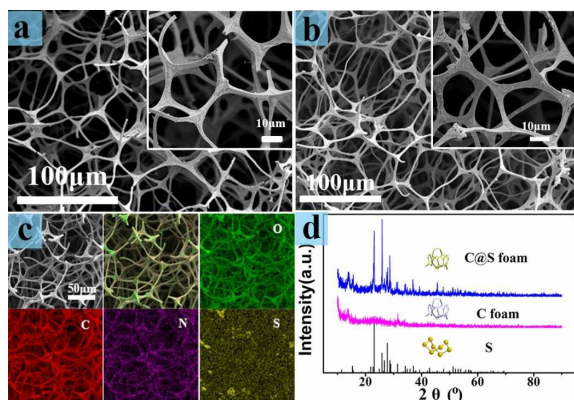


Fig. 2 The scanning electron microscopy image of the carbon foam (a) without and (b) with sulfur, (c) the C@S foam and corresponding EDS mapping for the element distribution. (d) XRD pattern of carbon foam and C@S foam.

The carbon foam (C foam) was developed by directly carbonizing melamine foam (MF) resin. The main component of MF is formaldehyde–melamine, which is a commercially available environmentally friendly polymer foam material.<sup>[31]</sup> The  $N_2$  adsorption–desorption isotherm of the C foam was conducted (Fig. S1), and it shows a Brunauer–Emmett–Teller (BET) specific surface area of  $52.96 \text{ m}^2 \text{ g}^{-1}$  and a large pore volume of  $2.03 \text{ cm}^3 \text{ g}^{-1}$ . The C foam-coated sulfur material (C@S foam) was fabricated through a facial solution immersion method (Fig. 1a). And the loading of sulfur approximate 1.2 mg. Good elasticity was observed in both the C foam and the C@S foam (Fig. 1b, c).

To further examine the structure and component of the C foam and C@S foam, we performed scanning electron microscopy and energy dispersive spectrometer mapping. As shown in Fig. 2a, the foam demonstrated a high slenderness ratio in the interconnection network architecture; such ratio determined the excellent elasticity of the foam.<sup>[31]</sup> The structure of the C foam was almost the same as that of the raw foam materials (Fig. S2). The sulfur cathode prepared through a simple solution impregnation method showed the same structure as that of the C foam. The elastic framework not only offered a shelter for sulfur but also prevented architecture deterioration resulting from volume expansion. Meanwhile, the interconnected framework could enhance the contact probability between the active sulfur and the electrolyte, thus potentially improving the use of active sulfur to some extent.<sup>[34]</sup> The thickness of the sulfur deposited on the C foam was approximately 300 nm (Fig. S3). The distance between adjacent skeletons was approximate  $50 \mu\text{m}$  before the battery assembling. However, the skeletons have been closer with an integral structure after battery assembling (Fig. S4). The result

of reducing distance is short the diffusion distance of polysulfides. The C foam comprised carbon, nitrogen, and oxygen. Part of the sulfur block was observed in the mapping pattern, as well as in the SEM pattern (Fig. S3). This result is consistent with low active material utilization. The X-ray diffraction (XRD) of the C foam with and without sulfur (Fig. 2) proved the good combination of sulfur and the C foam. The characteristic peaks of the orthorhombic phase of sulfur (JCPDS no. 08-0247) were observed in the characteristic XRD patterns of the C@S foam. This result indicated the existence of crystal sulfur.

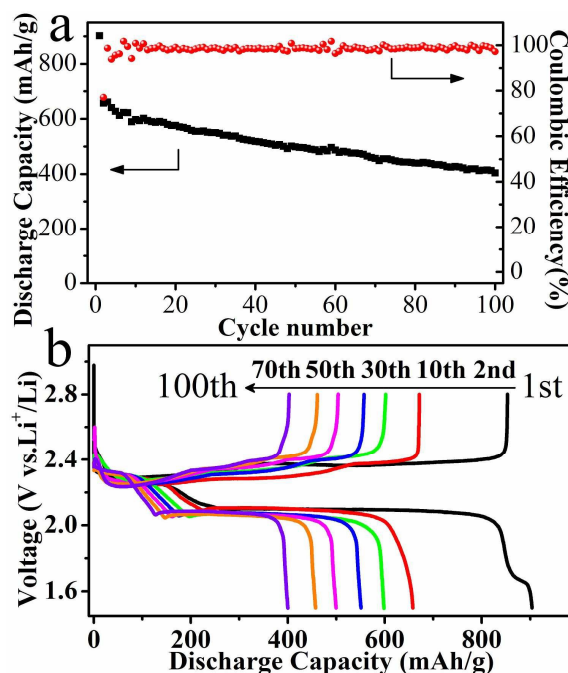


Fig. 3 The electrochemical performance of Li-S battery: (a) the cycle stability and coulombic efficiency, (b) the charge and discharge specific capacity at different cycles.

Figure 3 shows the galvanostatic charge–discharge curves of the Li–S battery with the C@S foam cathode at a 0.2 C rate. As shown in figure 3a, the first two discharge specific capacities reached  $893 \text{ mA h g}^{-1}$  and  $649 \text{ mA h g}^{-1}$ . The low discharge specific capacity is associated with the formation of block sulfur in the process of sulfur deposition in this work. Block sulfur with the low conductivity hinders the battery reaction largely. So the block sulfur turn into die sulfur in battery which has a little contribution to discharge capacity. In the absence of binder and coating, the sulfur deposited onto the surface of carbon foam skeleton is inevitable losing into electrolyte during the process of dissolution and deposition repeatedly. The coulombic efficiency approaching 98% was achieved after 100 cycles. The superior coulombic efficiency achieved in the galvanostatic charge–discharge curves may benefit from the addition of  $\text{LiNO}_3$ <sup>[35]</sup> and the special cathode material. On the one hand, a stable passivation layer formed by the oxidation of  $\text{LiNO}_3$  can efficiently slow down the reduction of polysulfide species at the lithium surface.<sup>[36]</sup> On the other hand, the good

flexibility of the cathode material can sustain the volume change during cycles. The two discharge plateaus were observed at 2.31 and 2.06 V, which corresponded to the reduction from S to  $S_4^{2-}$  and from  $S_4^{2-}$  to  $S^{2-}$ , respectively.<sup>[5]</sup> As the battery voltage approached 2.6 V in the charging process, the vertical voltage increased, thus indicating that cells

employing C@S cathodes can be completely charged without a significant shuttling effect.<sup>[37]</sup> However, the small knee point at 1.70 V in the first discharge curve may be associated with the irreversible reduction of  $LiNO_3$ , which only appeared in the first discharge curve.<sup>[38]</sup>

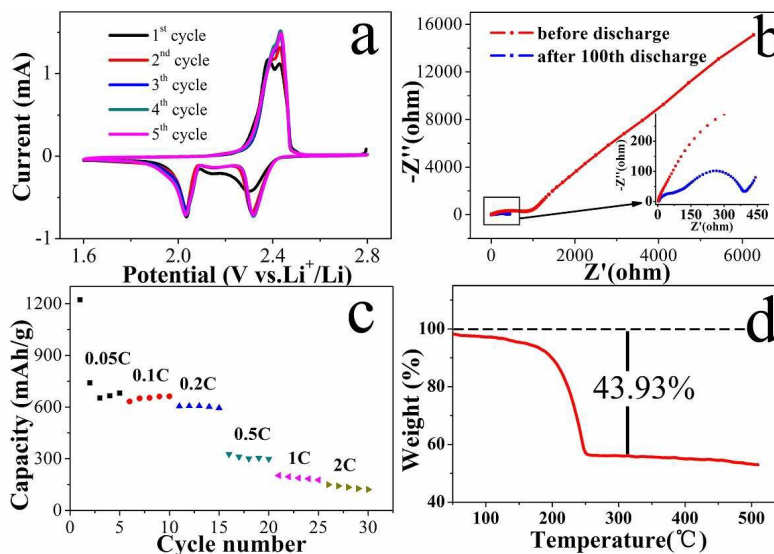


Fig 4. (a) The CV curves of the C@S foam cathode battery before discharge (b) Impedance plots of battery before and after cycling, (c) the rate performance of the battery and (d) the TG curves of C@S foam.

To investigate the charge–discharge behavior of the C@S cathodes, we conducted cyclic voltammetry (CV) measurements on the battery at a voltage range of 2.8 V to 1.6 V. As shown in Fig. 4a, the two main cathodic peaks at 2.31 and 2.06 V of the reduction curves are consistent with the two-step reduction of S, and the result corresponds to the charge–discharge curves. The difference of the cathodic peaks in the first and other cycles was ascribed to the rearrangement of active sulfur from its original positions to more energetically stable sites.<sup>[28]</sup> In addition, one oxidation peak with a small shoulder peak was observed in the CV curves in the first five cycles. This result indicated the oxidation of short-chain polysulfides to elemental sulfur or long-chain polysulfides.<sup>[39]</sup> The lack of obvious potential shifts in the other cycles confirmed the excellent reversibility and stability of the porous C@S foam cathode.<sup>[40]</sup>

Fig. 4b shows typical Nyquist plots of the Li–S battery with C@S cathode before and after 100 cycles in charged states. The Nyquist curves before the cycles were composed of one semicircle and a long inclined line, which represented the blocking character of the non-lithiated electrode.<sup>[41]</sup> After 100 cycles, the Nyquist curves comprised two depressed semicircles at the high frequency and middle frequency regions and a short inclined line in the low frequency regions. The semicircle at the middle frequency region reflected the charge transfer resistance and its relative capacitance at the phase interface.<sup>[42]</sup> In comparison with the AC impedance before the cycles, the semicircle after the cycles decreased obviously, which is in agreement with the rearrangement of

sulfur described above. In addition, the semicircle in the high frequency range was related to the formation of a solid electrolyte interface.<sup>[41]</sup> The incline in the low frequency region was related to the Warburg impedance.<sup>[43]</sup> The rate performance of the C@S foam battery at current densities ranging from 0.05 C to 2 C is shown in Fig. 4c. The C@S foam battery achieved a good performance rate at low current density and serious capacity decay at high current density. This result can be attributed to the high charge-transfer resistance and mass transport resistance in the cathode, which is a control step in the lower voltage plateau. The thermogravimetric analysis of the C@S foam revealed a sulfur content of approximately 43.93% which was based on the all weight of cathode.

In summary, we developed a simple and scalable C foam as a freestanding cathode for Li–S batteries. This material have shown good electrochemical performance. Therefore, we demonstrated the feasibility of C foam-supported sulfur cathode batteries without any conductive additive. The three-dimensional C foam with excellent flexibility presents great promise as an electrode material for emerging portable, flexible, and wearable electronics. Moreover, the advantages of the facile fabrication method and the commercially available material make them alternatives for the emerging flexible battery market. Meanwhile, the fabrication method of our cathode material will be suitable for large scale industrial production.



## Experimental

The porous carbon foam was fabricated by direct carbonization of melamine foam at 750 °C with a heating rate of 5 °C min<sup>-1</sup> under nitrogen atmosphere and annealing for about 1 h at the final temperature. Then the carbon foam was cut into desired shapes. The as-prepared carbon foam pieces was dipped into the ethanol solution saturated sulfur under the ultrasonic five minutes. Then the foam was transfer into vacuum oven at 70 °C with a vacuum condition. After repeating above process several times, the sulfur cathode with an excellent elasticity was accomplished.

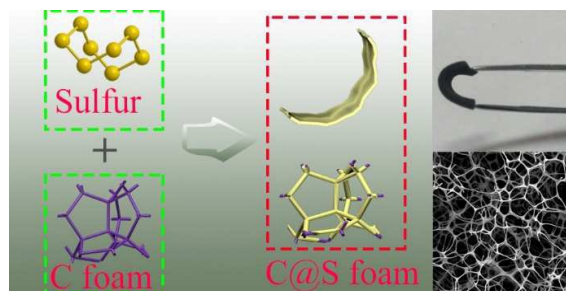
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