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# Preparation and electrochemical performance of a graphene-wrapped carbon/sulphur composite cathode

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**Abstract:** Graphene is used as a barrier film to suppress the "shuttle effect" and to improve the performance of activated carbon-sulphur hybrid cathode materials in a lithium-sulphur battery by forming a core-shell structure. Graphene wraps around the activated carbon-sulphur hybrid to form a core-shell structure, in which the porous carbon framework stores most of the sulphur and the graphene layer suppresses the movement of the soluble polysulfide in the electrolyte during charge-discharge, resulting in an improvement of capacity and cyclic stability during long-term cycling. Such a core-shell structure is formed by changing the hydrophilicity of graphene oxide during reduction, in which the hydrophobic graphene closely wraps around the hydrophobic carbon surface.

**Key Words:** Lithium-sulphur battery; Core-shell structure; Reduced graphene oxide; Carbon-sulphur compound

## 1 Introduction

In recent years, enormous effort has been made to develop batteries with a higher capacity and energy density to meet the requirement for all-electric vehicles and "green" energy storage[1]. Lithium-sulphur battery, newly emerged a few decades ago, occurs to people with its super high discharge capacity (1675 mAh/g) and theoretical energy density (2600 Wh/kg) [2]. Moreover, low cost and environmental-friendly sulphur electrode makes it promising in above applications [2-4]. However, its practical application is hindered by the inherent nature of sulphur cathode. For example, octasulphur (cyclo-$S_8$), the most stable allotrope of sulphur at room temperature, undergoes a series of structural and morphological changes during the charge-discharge process involving the formation of soluble lithium polysulfide $Li_2Sx$ ($3 \leq x \leq 8$) and insoluble $Li_2S_2$ and $Li_2S$. Soluble lithium polysulfide comes back and forth in electrolyte between electrodes during the charge-discharge process, accompanied with reduction and oxidation reaction, which is called "shuttle effect"[5-8], resulting in a loss of active material and spoiling of electrolyte, and thus leading to a poor cyclic performance and a low Coulombic efficiency.

In order to solve this problem, carbon materials, polymers and metal oxides framework are studied to store sulphur and limit dissolution of polysulfide in the electrolyte through both physical and chemical interactions [9-12]. Among them, carbon framework is believed to be more promising, and various carbons (such as porous carbon, carbon nanotube,

graphene, carbon fiber) have been frequently studied [13-29]. Carbon matrix not only provides room to hold sulphur and restrict the shuttle of polysulfide, but also improves the electrical conductivity of sulphur cathode. However, the suppression of dissolution of polysulfide and loss of active materials are unsatisfactory yet by using the simplex carbon structure. Thus, it is urgent to design a hybrid structure to improve it.

Herein, we proposed a hybrid structure to suppress the "shuttle effect" and improve the cyclic ability of the sulphur cathode. We used the activated carbon as the vessel to store the sulphur, and then, a graphene layer was coated on the activated carbon/sulphur hybrid (CS) as a barrier film forming a core-shell structure by a self-assembly method. Thus, the porous structure and such barrier layer conspire against the shuttle of polysulfide from the electrode, resulting in an improvement of capacity and cyclic performance. We also proposed a self-assembly approach that was made possible by the hydrophilicity change of graphene oxide (GO) by reduction. This hybrid achieves a proper loading of sulphur (43% mass fraction) and gives a stable electrochemical performance with an increasing discharge capacity of 300－400 mAh/g, compared to CS hybrid with a 42% sulphur loading. Also, an excellent rate capability is achieved. The improved electrochemical performance of this hybrid is attributed to the dual functions of the activated carbon and graphene as mentioned above.

## 2 Experimental

### 2.1 Sample preparation

In a typical experiment, activated carbon(XPF-01, Nanjing XF-NANO) and sulphur underwent a thermal treatment at 150 °C for 8 h under argon condition to enable sulphur melt into the pores, and then heated at 300 °C for 2 h to make the sulphur on external surface sublime to obtain CS hybrid. Proper amount of such hybrid was added into GO dispersion with a concentration of 2 mg/mL under strong sonication to form a uniform mixture since GO can be used as a new type of dispersant. Then, suitable amount reduction agent ($N_2H_4 \cdot H_2O$) was added in the above mixture, and GO was reduced into reduced graphene oxide (RGO) accompanied with the loss of oxygen-functional groups, resulting in a loss of hydrophilicity. Thus, the graphene layer certainly wrapped on the hydrophobic CS surface to obtain the core-shell structure as shown in Fig. 1. After centrifugation, filtration and drying, such product was produced and denoted as RGO@CS.

### 2.2 Structure characterization

Scanning electron microscopic (SEM) observations were conducted with Hitachi S-4800 (Hitachi, Japan). Transmission electron microscopic(TEM) observations were performed using JEM-2100F (JEOL, Japan) equipped with EDX which was used for elemental analysis. The X-ray diffraction (XRD) patterns were collected at room temperature using the reflection mode (D8 FOCUS, Cu *K*α radiation, λ=0.154nm). Nitrogen adsorption was measured by using a BEL mini-instrument, and the specific surface area was obtained by Brunauer-Emmett-Teller (BET) analyses of the adsorption isotherm. Raman spectra were recorded by a micro-Raman spectroscope (JY HR800) using 532.05 nm incident radiation and a 50× aperture. Thermogravimetric analysis (Rigaku, Japan) measurements were performed to calculate the sulphur content in the hybrid.

### 2.3 Electrochemical measurements

The RGO@CS hybrid powder was mixed with polyvinyldifluoride (PVDF) and super P carbon black in a weight ratio of 8:1:1 in N-Methyl-2-pyrrolidone (NMP) solvent to form a slurry. The slurry then was coated on an Al foil and dried under vacuum at 60 °C for 24 h. The foil was then cut to a circular pellet with a diameter of 15 mm used as cathode. The electrolyte was 1.0 mol/L LTFSI dissolved in DOL:DME (1:1 in volume). A 2032 coin cell was used to assemble the test cell in an Ar-filled glovebox (MBraun). Cyclic voltammetry (CV) was measured at a scan rate of 0.1 mV/s within a potential range of 1.5－3.0 V (vs. $Li^+$/Li). LAND galvanostatic charge/discharge instrument was used to test the rate performance.

## 3 Results and discussion

To characterize the morphology of RGO@CS, SEM and TEM are used.From the SEM image of RGO@CS shown in Fig. 2, we can clearly observe the graphene layer almost fully wrapped on the CS surface, resulting in a coarse surface.In comparison, the CS hybrid shows a very flat surface (Fig. 2a). Such layer prevents polysulfide and sulphur from dissolving into bulk electrolyte and improving the cyclic stability. Moreover, Fig. 2b also shows that some pores exist on the graphene layer, which can provide ion transportation channels, ensuring the power performance of the RGO@CS with a core-shell structure.

TEM images also prove the successful wrapping of RGO on the CS surface. The thin RGO layer with a winkled structure can be clearly and easily identified from the TEM images shown in Fig. 3a and 3b to be wrapped on the CS hybrid. The element mapping shown in Fig. 3c and 3d show the elemental distributions of carbon and sulphur in RGO@CS, respectively. It can be seen that the sulphur is mostly stored in the activated carbon and distributes uniformly. The TEM characterizations also show the RGO layer on the CS surface is very thin and very little sulphur exists on the graphene surface. SEM and TEM images show CS hybrid are well wrapped with RGO layer, hindering polysulfide from dissolving in electrolyte, which explains the improvement of its electrochemical performance in lithium sulphur batteries.

XRD results further confirm the effective wrapping of RGO on CS surface. Sulphur contained in the RGO@CS andCS hybrid is in a crystalline state compared with the XRD pattern of crystal sulphur. Besides, the intensity of diffraction peaks of sulphur contained in RGO@CS gradually decreases and the peaks become less resolved and broadened compared with those of pure sulphur and CS, suggesting that the outside RGO layer may induce the scattering of the X-ray, in accordance with the TEM and SEM observations.

The Raman spectra of the RGO@CS and CS are shown in Fig. 5. Vibrational mode which canbe assigned to sulphur is observed in RGO@CS and CS. This is quite the same as pure sulphur, which has several vibration signals below 500 $cm^{-1}$, indicating the sulphur is in the crystalline state. This result agrees well with the XRD results. Fig. 5 also shows the intensity ratio of *D* band and *G* band ($I_D/I_G$=1.76) of the RGO@CS is higher than those of RGO ($I_D/I_G$=1.52) and CS ($I_D/I_G$=1.42), owing to more defects appeared on the reduced graphene oxide layer as previously reported [30].
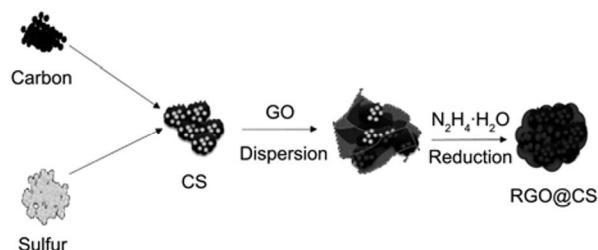


Fig. 1 Schematic process of the preparation of RGO@C.