



# Carboxyl grafted sulfur-expanded graphite composites as cathodes for lithium-sulfur batteries

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## ABSTRACT

Main challenging issues of sulfur as cathodes for lithium-sulfur (Li-S) batteries are poor conductivity of sulfur and dissolution of long-chain polysulfides ( $\text{Li}_2\text{S}_x$ ,  $x = 4$  to 8) formed during the redox processes. Herein, we demonstrate an advantageous method for embedding sulfur into the voids of the expanded graphite (EG) layers, forming S-EG composite. A further modification of the surface of S-EG with 3-cyanpropyl-trichlorosilane (CPS) was attempted to functionalize EG with carboxyl groups to form the carboxyl-grafted sulfur/expanded graphite composites, S-(EG-COOH). Thus, in addition to improvement in conductivity of the composites via the conductive framework of EG, the negatively charged carboxyl groups on EG could generate an environment to confine the polysulfide anions formed during charge/discharge cycling. It is demonstrated that modification of the carboxy groups on EG leads to an alteration of the surface properties of the material, including hydrophilicity and electrolyte wettability. Importantly, notable improvement in the initial discharge capacity ( $1058 \text{ mA h g}^{-1}$ ) and Coulombic efficiency (87.47%), and cyclability (capacity retention of 70% after 100 cycles) of sulfur indicates that carboxyl groups could relieve the dissolution of polysulfides and promote the charge transfer at the sulfur/electrolyte interface. High dispersion of sulfur in EG, good conductivity with the aid of EG, and fast Li diffusion are ascribed to be responsible for the superior electrochemical performance of S-(EG-COOH).

## 1. Introduction

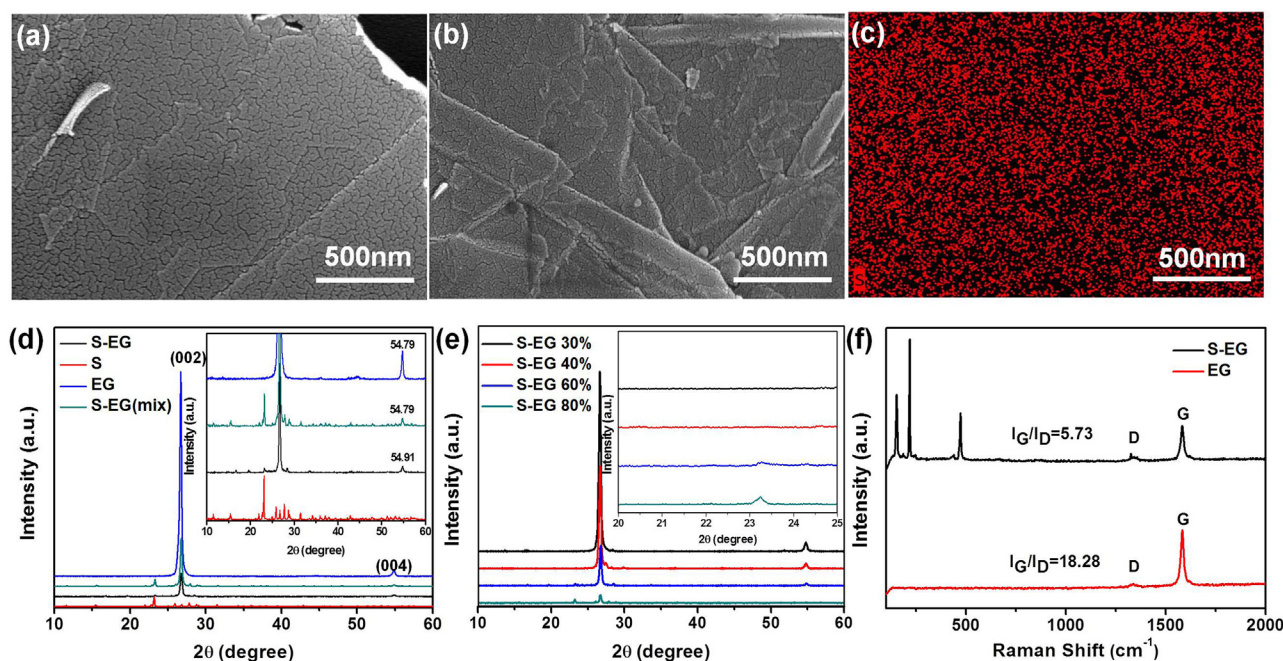
Sulfur as the cathode material in Li-S batteries has superior theoretical capacity ( $1672 \text{ mA h g}^{-1}$ ) and high energy density ( $2500 \text{ Wh kg}^{-1}$ ), resulting in consideration as cathode material for promising secondary batteries, in particular to meet the requirements of electric vehicles, storage for renewable energy, and advanced portable electronic devices [1–3]. However, there are still many challenging issues that impede Li-S batteries from practical commercialization and wide application, including the insulating nature of sulfur and  $\text{Li}_2\text{S}$ , high solubility of polysulfides formed in the charge/discharge process, and large volume change from lithiation/delithiation of sulfur. To improve the conductivity of the sulfur materials, mesoporous carbon was first introduced to encapsulate sulfur within the conductive channels [4]. Thereafter, various conductive materials, such as carbon nanotubes, graphene, and porous carbon, have been employed to embed sulfur [5]. On the other hand, Li-S batteries involve multi-electron transfer electrochemistry, which differs from the intercalation electrochemistry in most lithium ion batteries. A series of intermediates are formed during the charge/discharge process. Particularly, the high

order  $\text{Li}_2\text{S}_x$  species ( $4 \leq x \leq 8$ ), among those intermediates soluble in most of the organic electrolytes, is considered as a most critical issue to influence the utilization and Coulombic efficiency of sulfur. As a consequence, the sulfur electrode suffers substantial dissolution of the polysulfides, leading to rapid decay in the specific capacity and low efficiency. In order to overcome this issue, researchers have proposed a variety of different methods. Popular methods include using solid-state electrolyte [6–8], adding electrolyte additives [9–11], using permselective membranes [12], and devising improved cathode architecture [13–17] to confine the dissolution of polysulfide by either embedding sulfur in porous carbon matrices or implanting sulfur in conducting polymers [18, 19]. In particular, it has been suggested that the loss of polysulfides into electrolyte is associated with the weak interaction between the polar polysulfides and nonpolar carbon materials [20]. A series of conductive polar host materials have been developed, including heteroatom incorporated conjugated polymers, heteroatom doped carbon, transition metal oxides (or sulfides, carbides, and nitrides), metal organic frameworks (MOFs), etc. Under this circumstance, chemical interaction between the polysulfides and polar host materials could exist to immobilize the soluble sulfur species [21]. The

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**Fig. 1.** SEM images of (a) EG and (b) S-EG; (c) EDS mapping for S of S-EG; (d) XRD patterns of S, EG, S + EG, and S-EG; (e) XRD patterns of S-EG samples with 30, 40, 60, and 80 wt% of sulfur; (f) Raman spectra of EG and S-EG.

cyclability of sulfur could be significantly improved by the formation of chemical bonding of the sulfur species to the oxygen-containing groups on the polar matrix. Nevertheless, an efficient and economic approach is still urgently needed for the fabrication of the sulfur cathode materials for Li-S batteries.

So far, surface engineering of the conductive host materials with functional organic molecules has hardly been attempted to improve the electrochemical performance of sulfur. In this report, we propose an effective method to improve the conductivity of the electrode material and to alleviate polysulfide dissolution by grafting carboxyl groups onto the expanded graphite (EG) embedded with sulfur. Sulfur can be embedded into the structural gaps of EG by heating treatment [22]. Thus, EG could not only serve as micro-containers for sulfur, but also provide a conductive framework to improve the electrical conductivity of the S-embedded EG (S-EG) [23, 24]. We further intensively modify the surface of S-EG with 3-cyanpropyl-trichlorosilane (CPS), which is a common silane coupling agent and could react with the oxygen-containing groups on the surface of EG [25, 26]. Hydrolysis of the cyanide groups on the surface of the modified S-EG leads to the formation of carboxyl groups on the surface of S-EG, resulting in the formation of carboxyl group grafted S-EG, S-(EG-COOH). The grafted carboxyl groups are expected to generate an environment to alleviate polysulfide dissolution effectively via the electrostatic repulsion between the carboxyl groups and polysulfides. It is demonstrated that the electrochemical performance of the embedded sulfur can be greatly improved with the aid of conductive EG and confinement of carboxyl groups to polysulfides anions.

## 2. Experimental

### 2.1. Synthesis of S-EG composites

The expandable graphite was rapidly expanded at 900 °C for 3 min in an air atmosphere to form EG. Then the EG and sulfur were mixed in various weight ratios. The mixtures were heated to 150 °C for 6 h in a nitrogen atmosphere and S-EG composites were obtained.

### 2.2. Synthesis of S-(EG-COOH) composites

The prepared S-EG was immersed in a 2% CPS solution at room temperature overnight. Then, the resulting powder was collected by filtration, and rinsed with chloroform and ethanol, respectively. Next, the cyanide groups on the surface of EG were hydrolyzed to generate carboxyl groups in an acidic solution to obtain the S-(EG-COOH) composites.

### 2.3. Characterization of sample

The crystallographic structure and phase of S-EG composites and S-(EG-COOH) composites were characterized with a power X-ray diffractometer (XRD, MiniFlex 600) using a Cu K $\alpha$  radiation source with the 2 $\theta$  range of 10–60°. A Raman spectrometer (HR 800), equipped with a He-Ne laser transmitting at 633 nm, was used to confirm possible defect formation. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi (Thermo Scientific) using a standard Mg K $\alpha$  X-ray source. The results of contact angle data (JC2000DS) confirmed the wettability values of the electrolyte.

The electrochemical measurements were carried out in 2032 coin-type cells. The cathodic electrodes were prepared by mixing active materials, polyvinylidene fluoride (PVDF) and conducting additive (Super P), at a weight ratio of 8:1:1. The mixture was coated on aluminum foil and dried at 60 °C for 12 h in a vacuum oven. The coin cells were assembled with the electrolyte of 1 M LITFSI in a mixture of 1, 2-dimethoxy ethane (DME) and 1, 3-dioxolane (DOL) (50:50, v:v) in an argon-filled glove box. The coin cells were tested between 1.5 V and 3 V on a LAND CT2001A battery testing system at room temperature.

## 3. Results and discussion

Sulfur can be loaded into EG with via a melt-diffusion strategy to form the composite [22]. Under the heating treatment conditions, the sulfur could be highly dispersed into the layers of EG. The comparison of the SEM graphs of EG and S-EG with sulfur loading content of 60 wt% reveals that no obvious large sulfur masses could be observed for S-EG, as indicated in Fig. 1a and b, only few small particles of sulfur are

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