



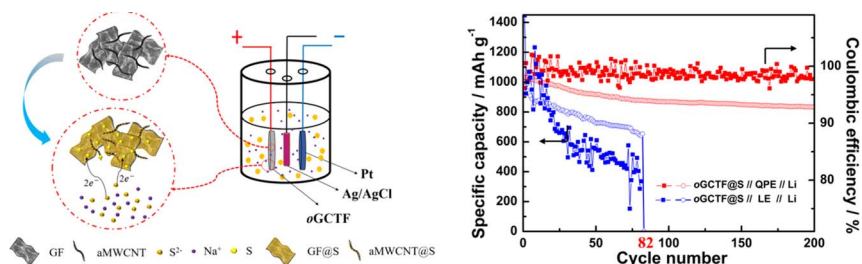
# High-performance lithium-sulfur batteries based on self-supporting graphene/carbon nanotube foam@sulfur composite cathode and quasi-solid-state polymer electrolyte



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## GRAPHICAL ABSTRACT



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## ABSTRACT

The dissolution and shuttle of the intermediate lithium polysulfides are major issues which restrict practicality of lithium-sulfur batteries. Herein, self-supporting graphene/acid-treated multi-walled carbon nanotube organic foam-supported sulfur (oGCTF@S) composites are fabricated by solvothermal reaction followed by electrochemical deposition. The oGCTF@S composites can provide high electronic conductivity and much void space for accommodating volume change of sulfur and confine dissolution of the polysulfides by physical adsorption. In addition, a novel quasi-solid-state polymer electrolyte (QPE) of poly(butyl acrylate)/poly(ethylene glycol) diacrylate (P(BA-co-PEGDA))/LiTFSI-DOL/DME is prepared to further suppress the polysulfides shuttle through chemical adsorption with oxygen-containing functional groups. The lithium-sulfur battery assembled by oGCTF@S composites cathode and QPE shows a high initial discharge capacity of  $1033 \text{ mAh g}^{-1}$ , and the capacity can retain  $834 \text{ mAh g}^{-1}$  after 200 cycles at 0.1 C, which is much more stable than that with the commercial separator and liquid electrolyte (LE).

## 1. Introduction

Lithium-sulfur battery, the most promising candidate for storage devices, has been extensively studied not only due to the natural abundance, nontoxicity, and low cost of sulfur, but because of the high specific capacity ( $1673 \text{ mAh g}^{-1}$ ) of sulfur [1–4]. However, there are

still some major issues that impede the widespread commercialization of Li-S battery. The three key problems are the intrinsic electrical and ionic insulation of sulfur, the dissolution of the intermediate lithium polysulfides ( $\text{Li}_2\text{S}_n$ ,  $4 \leq n \leq 8$ ) and the dendrite of lithium anode [5–9].

Typically, to address the poor conductivity of sulfur cathode, the

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most common strategy is to combine sulfur with conductive materials, such as carbon materials [10–28], polymer materials [29–37] and metallic compound [38–41]. Among them, the self-supporting graphene foam (GF) as a new kind of carbon materials is highly favored because of its novel three-dimensional (3D) structure, large accessible surface and integrated conductive network [42–47]. Besides, the 3D framework can provide large amount of void space to accommodate the significant change of sulfur in volume and constrain polysulfides, which enhances the cycling stability. However, the oxygen-containing functional groups and defects in GF derived from the hydrothermal process worsen its electrical conductivity. Fortunately, the hybrid foams [45–47] combined with carbon nanotube help to offset the inferiority of GF in the practical application of Li-S batteries, further improving the rate performance and cycling stability.

Another major problem, shuttling effect, can be settled from two aspects, physical and chemical adsorptions. Porous or element-doped carbon materials [11–15,24,39], interlayer between cathode and separator [9,48–54], conductive polymer coating [29,33,45,46] are all effective ways to suppress the shuttling. Apart from all above, gel polymer electrolyte [8,55–64] can work similarly to physically constrain the polysulfides. In addition, the solvent volatilization and leakage of the liquid electrolyte can be retarded and enhance the safety of the Li-S battery. However, the polysulfides confined in open structure can still dissolve into the liquid electrolyte, leading to inevitable loss of the active materials and the redox shuttle effect during long cycling. Thus, we need stronger interactions, such as the covalent attachment or polar adsorption, to restrict the polysulfides. The ideal interaction between the lithium ions in the polysulfides and the oxygen donor atoms in ester (R-COO-R') or ether (R-O-R') groups has been proven to be a good choice [55,59].

Herein, we prepared a graphene nanosheets (GNS)/acid-treated multi-walled carbon nanotubes (aMWCNT) organic foams (oGCTF) by solvothermal reaction. Afterwards, self-supporting GNS/aMWCNT organic foam-supported sulfur (oGCTF@S) composites were obtained by electrochemical deposition. The electrochemical deposition process of the oGCTF@S composites is illustrated in Fig. 1. The GNS/aMWCNT hybrid foam can efficiently boost electrical conductivity and further benefit the construction of 3D conductive network for oGCTF@S cathode. In addition, the 3D self-supporting architecture can act as a non-binder and non-current collector electrode, which greatly enhance the energy density and avoid the poor electric connection between the active material and the current collector. We prepared a poly(butyl acrylate)/poly(ethylene glycol) diacrylate (P(BA-co-PEGDA)) membrane and obtained a novel quasi-solid-state polymer electrolyte (QPE) of P(BA-co-PEGDA)/LiTFSI-DOL/DME to substitute liquid electrolyte (LE). The highly cross-linked P(BA-co-PEGDA) with functional groups

(R-O-R' and R-COO-R') can confine the polysulfides through physical and chemical adsorption, improving the stability of the batteries. As a result, the as-assembled oGCTF@S//QPE//Li lithium-sulfur battery exhibited encouraging electrochemical performance, especially the high specific capacity (1033 mAh g<sup>-1</sup>) and long-term cycle stability (80.6% capacity retention after 200 cycles at 0.1 C).

## 2. Experimental

### 2.1. Preparation of oGCTF@S cathode

The graphene/acid-treated multi-walled carbon nanotube organic foam (oGCTF) was prepared by the solvothermal method described in detail in a precious report of our group [46]. The preparation process of oGCTF is shown in Supporting Information. The as-prepared cylindrical oGCTF foams were cut into slices for the following steps. Then, the electrochemical deposition of oGCTF@S was conducted with a three-electrode cell in a deionized water/N,N-dimethyl acetamide (DMAc) (1/1, v/v) solution containing 0.2 M Na<sub>2</sub>S·9H<sub>2</sub>O using a CHI 760C electrochemical workstation. The working electrode was the above oGCTF foam slice and the counter electrode was the Pt flake with surface area of 4 cm<sup>2</sup>. The sulfur was in-situ electrodeposited into the oGCTF at a constant potential of 1.4 V vs. Ag/AgCl for different charge quantity (15C, 25C and 35C) named as oGCTF@S-1, oGCTF@S-2 and oGCTF@S-3, respectively. Finally, the resulting oGCTF@S were washed with deionized water for several times and dried under 60 °C for 12 h before using as the cathode.

### 2.2. Preparation of the P(BA-co-PEGDA)/LiTFSI-DOL/DME quasi-solid-state electrolyte

The poly(butyl acrylate)/poly(ethylene glycol) diacrylate (P(BA-co-PEGDA)) membranes were synthesized by radical polymerization. Firstly, 0.1 wt% benzoyl peroxide (BPO) was dissolved in 20 g butyl acrylate (BA) under stirring and the pre-polymerization was maintained at 85 °C for a certain time until the reagent became viscous. Then, cross-linking agent poly(ethylene glycol)diacrylate (PEGDA) with different contents (5 wt%, 10 wt%, 15 wt% and 20 wt%) and 0.1 wt% BPO were added into the above precursor solution respectively and bubbled with argon gas to get rid of oxygen. After that, the above solution was injected into a mold of 100 × 100 × 0.1 mm<sup>3</sup> and evacuated to remove bubbles. Finally, the reaction was maintained at 45 °C for 20 h, then 100 °C for 2 h to obtain the P(BA-co-PEGDA) membrane. The as-prepared membranes were washed with ethanol to remove the unreacted monomers and then dried in oven under 60 °C. The dried P(BA-co-PEGDA) membranes were immersed in 1 M LiTFSI-DOL/DME

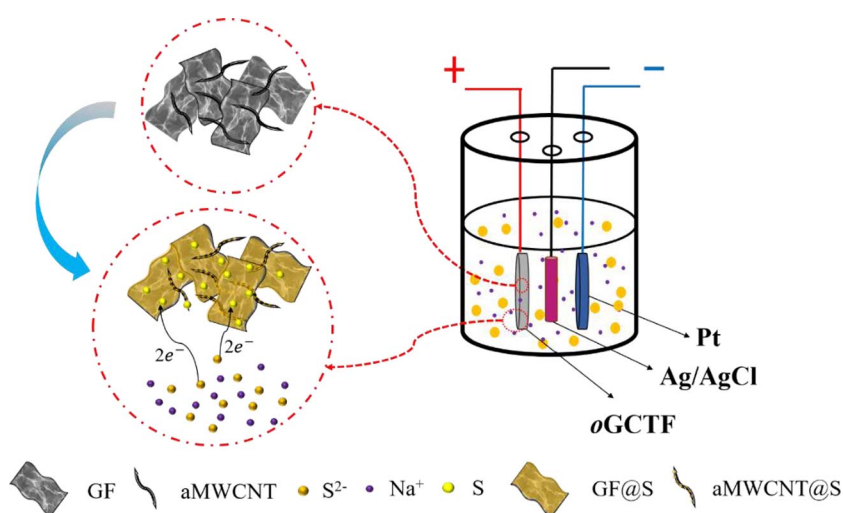


Fig. 1. Schematic illustration of the electrochemical deposition process of the self-supporting oGCTF@S composites.

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