



High areal capacity of Li-S batteries enabled by freestanding CNF/rGO electrode with high loading of lithium polysulfide



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ABSTRACT

Lithium-Sulfur (Li-S) batteries, the most promising next-generation batteries for their high theoretical capacity, are still hindered by several obstacles mainly due to the effect of polysulfide shuttle. Recently, considerable progress has been made to improve the specific capacity and cycling life of the Li-S batteries, but most demonstrations are typically based on thin electrode with limited areal sulfur loading. Herein, we demonstrate a Li-S battery with electrospun carbon nanofiber/reduced graphene oxide (CNF/rGO) as the binder-free and self-standing host for lithium polysulfide-containing liquid active materials in the cathode. The matrix of intertwined long CNF networks with uniformly distributed rGO pieces promotes the long-range high-rate charge transfers in three dimensions, and provides sufficient porous spaces for polysulfide uptake. Plus the mechanical flexibility of the CNF/rGO membrane, thick electrode with high areal sulfur loading (20.3 mg/cm²) and high areal specific capacity (15.5 mAh/cm²) is demonstrated by a Li-S pouch cell with stable cycling performances.

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1. Introduction

Next-generation advanced energy-storage systems for portable devices, electric vehicles, and grid storage must fulfill several requirements: high energy, high power, long life, low cost, reliable safety, and environmental benignity [1]. Rechargeable lithium-ion batteries, through achieved great success in the past two decades, fall short of the high energy/power and low cost [2–5]. Lithium-sulfur (Li-S) batteries have been regarded as the top candidates and have received intensive attention, due to the fact that sulfur can deliver a high theoretical capacity of 1672 mAh/g and a high theoretical energy density of 2600 Wh/kg, which are 3 to 5 times higher than Li-ion batteries (e.g. 387 Wh/kg of commercial LiCoO₂/C battery). In addition, sulfur is inexpensive and readily abundant in the Earth's crust, which make Li-S batteries particularly attractive [6,7].

Nevertheless, the commercialization of Li-S batteries is hindered by the low utilization of electrode active materials due to the low conductivity of sulfur, the rapid capacity fading resulting from the shuttling of soluble polysulfide species in the electrolyte

between cathode and anode, and safety issues arising from the dendritic growth at the Li metal anode [8–11]. Li-S batteries feature a two quasi-plateau discharge/charge voltage profile. During the cycling, a series of intermediate long-chain lithium polysulfides (Li₂S₈ ↔ Li₂S₆ ↔ Li₂S₄) dissolve into the ether-based electrolyte, diffuse towards the anode, and are reduced into insoluble and short-chain sulfide species (Li₂S₂/Li₂S) on the surface of the Li metal, leading to the rapid capacity fading [12,13]. Meanwhile, the repeated deposition of the insoluble species (S₈ and Li₂S₂/Li₂S) and dissolution of the high-order polysulfides at the cathode side further deteriorate the cell kinetics and exacerbate the poor cycling performances.

Many strategies have been developed to mitigate these issues. The most popular approach is using carbon host materials to trap sulfur and suppress the dissolution of polysulfides, aiming to impede the polysulfide shuttle [14–16]. These carbonaceous materials mainly include 0D carbon porous particles [17], 1D carbon nanotubes/nanofibers [18–25], 2D graphene and graphene oxides [10,26–29], and 3D carbons with various scales of porous structures (micro-, meso-, and macro-scale) [30–34]. Other than the physical restriction of the polysulfides by the carbonaceous materials, chemical anchoring of the polysulfides species was also reported by adding different dopants, polar chemicals, or surface modifications in the electrode [35–40].

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However, most of the sophisticated architectures will not satisfy the need of practical high energy density Li-S batteries when the areal sulfur loading is about ~ 2 mg/cm² as reported in many works, even though impressive specific capacity is achieved [41,42]. This issue promotes the recent attention in research community to pursue high areal capacity of Li-S batteries with high sulfur loading [43–48]. Qie et al. presented an electrode with sulfur splinted between six layers of activated CNF membranes, and achieved areal sulfur loading of 11.4 mg/cm² and areal capacity of 11.3 mAh/cm² [43]. Yuan et al. reported a CNT-S paper electrode with sulfur loading of 6.3 mg/cm², and can have three layers stacked together for areal sulfur loading of 17.3 mg/cm² and areal capacity up to 15.1 mAh/cm² [44]. Fang et al. prepared a hollow nanofiber foam current collector for accommodating CNT-carbon black-S hybrid materials, yielding a high sulfur loading weight of 21.2 mg/cm² [45]. Despite these progresses, challenges in facile fabrication of low-cost electrode materials and scalable demonstration of high sulfur-loading Li-S batteries still remain to be addressed.

Herein, we designed a Li-S battery with electrospun carbon nanofiber/reduced graphene oxide (CNF/rGO) as the binder-free and self-standing conductive frameworks for hosting lithium polysulfide-containing liquid active materials. The benefits of this design are as follows: (1) the CNF/rGO matrix provides the mechanical flexibility and 3D long-range charge transfer, so that the freestanding electrode eliminates the use of polymer binder and is capable of absorbing large amount of polysulfides or sulfur in thick membrane without obvious degradation in the electrochemical performances; (2) the highly porous CNF/rGO matrix allows the sufficient absorption of electrolyte/catholyte in the cathode and slows down the diffusion of the polysulfide shuttling. As a result, assembled Li-S coin cells with CNF/rGO achieved stable cycling life and high rate performances (up to 2C rate) with sulfur weight percentages of 49 wt% and 56 wt% relative to the total electrode weight. Furthermore, thick electrode with high areal sulfur loading (20.3 mg/cm²) and high areal specific capacity (15.5 mAh/cm²) was demonstrated by a Li-S pouch cell with stable cycling performances.

2. Experimental

2.1. Synthesis of CNF/rGO membrane

The precursor solution for electrospinning was prepared by dissolving 15 mg Graphene Oxide in 18 ml N,N-dimethylformamide (DMF) by sonication for 30 min. Then, 1.8 g polyacrylonitrile (PAN, Mw = 150,000, J&K Chemical) was added and stirred at 80 °C for 12 h. The final solution was loaded into a 20 ml syringe with a 22-gauge metallic needle. The flow rate was 1.0 ml/h, with a high voltage of 13 kV was applied to the needle. The distance between the needle and the collector was about 15 cm. Humidity and temperature of the atmosphere were controlled at about 15% and 20 °C, respectively. The as-electrospun membrane was peeled off from the collector after about 5 hours, and was stabilized at 200 °C for 1 h at a rate of 5 °C/min. The porous carbon nanofibers were finally obtained after calcinating at 1100 °C for 12 h at a rate of 5 °C/min in Ar atmosphere.

2.2. Preparation of polysulfide catholyte

The liquid polysulfide catholyte prepared by directly reacting elemental sulfur with stoichiometric Li₂S (S:Li₂S = 5:1, in molar ratio) in a blank electrolyte at 60 °C for 24 h to form 2 M Li₂S₆ (molar ratio, calculated based on S atom). The blank electrolyte was prepared by dissolving 1 M LiTFSI (Sigma Aldrich, 99.995%) and 0.5 M LiNO₃ (Alfa Aesar, 99.999%) in DOL:DME (1:1, volume ratio).

2.3. Materials Characterization

X-ray diffraction data were collected on a Panalytical instrument (X'Pert 3 Powder). The morphology of the carbon nanofiber webs was characterized by a scanning electron microscope (Hitachi SU8020) equipped with an energy dispersive X-ray spectrometer (EDX). For Transmission Electron Microscopy (FEI/Tecnaï G2 F20), the CNF/rGO sample was dispersed in ethanol and drop-casted to a Cu TEM grid. Nitrogen-sorption analysis was carried out to investigate the pore-size distribution, pore volume, and specific surface area of the product.

2.4. Electrochemistry

CR2032 coin cells were assembled in an argon-filled glove box with water and oxygen content kept below 0.1 ppm for testing Li/polysulfide batteries. The rGO/CNF membrane was cut into thin circular plates with about 1.5 mg weight. The coin cell was assembled with thin circular rGO/CNF plate soaked with 2 M Li₂S₆ catholyte as the cathode, a porous membrane (Celgard 2400) as the separator, and the lithium foil as the anode. The Li/polysulfide cells were firstly discharged to 1.6 V, then cycled between 1.6–2.8 V at different rates (1 C = 1672 mA/g_{sulfur}). Electrochemical impedance spectra (EIS) were measured from 0.01 to 100 kHz with a voltage amplitude of 5 mV. Cycle voltammetry data was collected between 1.6 and 2.8 V at a scan rate of 0.2 mV/s. The specific capacities were calculated based on the mass of sulfur in the cathode. The pouch cell was assembled with Al and Ni tabs as electrical connection for cathode and anode, respectively. A thick CNF/rGO membrane (~ 290 μ m) was loaded with 950 μ L of 2 M Li₂S₆ catholyte for the cathode, correspondent to a areal sulfur loading of 20.3 mg/cm².

3. Results and Discussion

Thick electrode with high areal sulfur loading is rarely achieved by conventional electrode design through doctor blade-coating the mixture of active materials, polymer binder and conductive additives. First, the electrode membrane is prone to form crack or debond from the metal current collector when increasing the thickness. Second, the poor conductivity of the thick electrode could severely deteriorate the electrochemical performances. It has been demonstrated that freestanding conductive porous cathode could be a highly promising approach to achieving high areal capacity, high sulfur loading, and high energy density [43,48]. Therefore, we proposed a Li-S battery with the configuration illustrated as Fig. 1 a. 3D porous membrane of intertwined CNF and rGO soaked with liquid polysulfide catholyte (Li₂S₆ dissolved in blank electrolyte) is utilized as the binder-free and self-standing electrode. The hierarchical interlinked ultra-long CNFs form a long-range conductive matrix providing efficient electron transport and multiple conductive pathways for the insulating discharge/charge products. Furthermore, the sufficient void spaces can act as reservoirs for the catholyte uptake, allow good penetration of the electrolyte, and accommodate volume changes of active materials during the cycling. The rGO is further added to increase the surface area and conductivity of the electrode, so as to improve the catholyte uptake volume and the electrochemical performances.

Electrospinning is adopted for the synthesis of the 3D porous CNF/rGO membrane, since it can be easily scaled up for the manufacture of long CNF networks with large area. GO is added in the precursor mixture for electrospinning. GO can be uniformly dispersed in the precursor (see the gray mixture in Fig. 1 b) since it is soluble in DMF (a polar aprotic solvent), and therefore would not block the needle during the electrospinning. After the calcination at 1100 °C, not only that the polymer PAN nanofibers will be converted into partially graphitized CNFs, but also that the GO will

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