



## Research paper

## Towards flexible lithium-sulfur battery from natural cotton textile



Zan Gao, Yunya Zhang, Ningning Song, Xiaodong Li\*

Department of Mechanical and Aerospace Engineering, University of Virginia, 122 Engineer's Way, Charlottesville, VA 22904-4746, USA

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## ABSTRACT

The future wearable/portable electronics need flexible power sources with higher storage capability. Lithium-sulfur (Li-S) battery is very promising for the development of next-generation high-energy battery due to its ultra-high theoretical capacity. However, the development of flexible Li-S battery has been plagued by its fast capacity decay and lack of suitable flexible substrates. Herein, a conductive activated cotton textile (ACT) with porous tubular structure was first derived from natural cotton textile to load sulfur, which was further wrapped with partially reduced graphene oxide (ACT/S-rGO) to immobilize lithium polysulfides. Meanwhile, the partially reduced graphene oxide nanosheets could be served as a conductive coating, which further mitigated the poor conductivity of sulfur and enabled fast electron transportation along ACT fibers. Furthermore, a KOH-activated ACT with micropore size distribution was inserted between cathode and separator to mitigate the “shuttle effect” of polysulfides. Finally, the assembled ACT/S-rGO cathode with porous ACT interlayer exhibited an exceptional rate capability and durable cyclic performance (with a well-retained capacity of  $\sim 1016 \text{ mAh g}^{-1}$  even after 200 cycles). A flexible Li-S cell with ACT/S-rGO as a cathode was also assembled to demonstrate its superior potential as flexible power sources for future wearable electronic devices.

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## 1. Introduction

Rechargeable lithium-ion batteries have largely revolutionized modern portable and mobile electronics devices and are still the most important energy storage systems, because of their high energy efficiency and long lifespan [1,2]. However, traditional electrode materials (such as  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$ ) have almost reached their theoretical limit, which cannot meet the increasing needs for fields that demand higher energy storage, such as electric vehicles and grid storage [3,4]. Therefore, it is necessary to explore new electrode materials and new redox chemistries for the development of next-generation batteries [5,6]. Lithium-sulfur (Li-S) battery is very promising for the development of next-generation high-energy battery because of its ultra-high theoretical capacity ( $\sim 1650 \text{ mAh g}^{-1}$ ), outstanding specific energy ( $\sim 2654 \text{ Wh Kg}^{-1}$ ), natural abundance, as well as environmental friendliness [7,8]. More encouragingly, some reported Li-S batteries have demonstrated superior practical capacity ( $\sim 550 \text{ mAh g}^{-1}$ ), more than twice of the state of the art lithium-ion batteries ( $\sim 180 \text{ mAh g}^{-1}$ ) [9,10].

However, despite the aforementioned advantages, Li-S battery manufacturing still encounters several roadblocks, including low sulfur utilization, severe capacity fading, poor cycling life and bad coulombic efficiency [11–14], which can be ascribed to the fundamentally different chemistry of Li-S batteries. For instances, in the Li-S system, sulfur usually undergoes a series of compositional and structural changes, including the formation of soluble lithium polysulfides ( $\text{Li}_2\text{S}_8$ ,  $\text{Li}_2\text{S}_6$ ,  $\text{Li}_2\text{S}_4$ , and  $\text{Li}_2\text{S}_3$ ) and insoluble lithium sulfides ( $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ ) [15]. Specifically, the dissolution of polysulfides often leads to the low utilization of sulfur, fast capacity fading, and serious “shuttle effect”, resulting in poor coulombic efficiency [16]. Additionally, the poor conductivity of both sulfur and the formed insoluble lithium sulfides jointly increase the reaction resistance, leading to poor utilization of active sulfur and bad cycling reversibility [17]. Furthermore, a large volume expansion up to 80% usually occurs during the conversion reaction from sulfur to lithium sulfide [18].

To date, various strategies have been explored to push up the potential of Li-S systems. For instances, numerous efforts have been devoted to hybridizing sulfur particles with various carbon materials (such as activated carbons [19,20], micro-/mesoporous carbon [21–24], CNTs [25], graphene [26,27], carbon fibers [28]) or conducting polymer (polyaniline [29]) to mitigate the poor conductivity of sulfur, or endowing the sulfur host materials with high porosity to retard the dissolution of polysulfides and buffer

\* Corresponding author.

E-mail address: [xl3p@virginia.edu](mailto:xl3p@virginia.edu) (X. Li).

the volume change. In addition, some other attempts, such as designing nanostructured cathode, adding additives ( $\text{LiNO}_3$ ) into the electrolyte, and optimizing cell configuration, have also been performed to suppress the “shuttle effect”, improve coulombic efficiency and extend the lifespan of lithium-sulfur systems [30–34]. Recently, graphene oxides (GO) were also employed as a sulfur immobilizer in GO/S composite cathode to prevent the dissolution of polysulfides through the strong chemical bonding between sulfur and the rich functional groups of GO [35–37]. Furthermore, the future portable/wearable electronic devices will be flexible and more functional, which definitely require the corresponding flexible power supplies with larger energy storage capacities. Recently, many efforts have been devoted to developing flexible Li-S batteries by incorporation sulfur with flexible substrates (such as carbon paper [38], mesoporous graphene paper [39], three-dimensional (3D) carbonaceous aerogel [40] or porous polymer sheets [41]), which hold great promise for next-generation flexible power sources because of their superior energy density than that of lithium-ion batteries [42]. Our previous studies have demonstrated that the activated cotton textile (ACT) converted from cotton textile could be an excellent platform for constructing flexible energy systems (e.g. flexible supercapacitors and flexible lithium-ion batteries) due to their excellent conductivity and eminent flexibility [43,44]. Recently, cotton derived carbon materials have been reported for both supercapacitor and Li-S battery applications [45–48]. However, to the best of our knowledge, ACTs have not been explored for flexible Li-S batteries. High energy flexible Li-S batteries can be integrated with solar cells to form self-sustained power sources, which holds a promise for future outdoor sensors and unmanned devices [49–51].

Herein, porous ACT fibers with tubular hollow structure were firstly prepared by a simple dipping, drying, and annealing process [52]. Sulfur nanoparticles were further infiltrated into ACT fibers via a simple heat treatment process in a sealed autoclave at the temperature of  $156^\circ\text{C}$ , where sulfur has the lowest viscosity, ensuring the fully penetration of sulfur into the pores and inner cavities of ACT fibers. The unique porous tubular structure of ACT fiber helped the infiltration of sulfur, finally enabling a high sulfur loading of  $\sim 5.5\text{ mg cm}^{-2}$ . The porous hollow structure of ACTs also helped to trap the formed polysulfides and facilitated fast lithium-ion transport during the electrochemical reaction processes. To effectively suppress the dissolution of polysulfides, the prepared ACT/S fibers were further wrapped with graphene oxide sheets, and then thermally treated at  $200^\circ\text{C}$  for 2 h to partially reduce GO to form ACT/S-reduced graphene oxide (ACT/S-rGO) composite, which demonstrated a strong capability to retard the dissolution of polysulfides through strong chemical bonding between polysulfides and the surface functional groups of rGO. Furthermore, a piece of KOH-activated ACT with hierarchical porous structure and micropore size distribution was cemented between the ACT/S-rGO cathode and the separator to serve as an interlayer with the purpose to trap polysulfides and mitigate the “shuttle effect” of polysulfides between cathode and anode. Finally, the ACT/S-rGO cell with porous ACT interlayer exhibited an exceptional capacity increasing (from 3th cycle  $\sim 852\text{ mAh g}^{-1}$  to 150th cycle  $\sim 1037\text{ mAh g}^{-1}$ ), impressive rate performance (the discharge capacity retained well even with current density increasing from 0.3 to  $2.4\text{ mA cm}^{-2}$ ) and doubled cyclic stability (compared with the 100 cycles of ACT/S cell). A flexible Li-S cell was also assembled to demonstrate its practical usage as a flexible power source, which kept its high capacity and excellent mechanical stability even after repeated bending processes, holding great promise for fabricating next-generation flexible power supply for portable/wearable electronics.

## 2. Experimental section

### 2.1. Preparation of Flexible ACT/S-rGO Hybrid Cathode Electrode

All chemicals are analytical grade and were used after purchasing without further purification. Activation of cotton T-shirt into ACTs followed our previously established method [53]. Typically, a piece of cotton textile was soaked in 1 M NaF solution and then dried overnight in the oven. The NaF treated cotton textile was thermally treated at  $1000^\circ\text{C}$  for 1 h in a horizontal tube furnace under a continuous argon gas flow (300 sccm). After cooling, the as-obtained ACTs were washed with distilled water to remove residual NaF and then dried at  $80^\circ\text{C}$  for 12 h. A piece of ACT ( $1.5\text{ cm} \times 2\text{ cm}$ ) was first loaded with sulfur powders and then thermally treated at  $156^\circ\text{C}$  for 10 h in a sealed autoclave to infiltrate sulfur into the inner pores and cavities of the ACT. After such thermal treatment, sulfur nanoparticles were homogeneously anchored on or penetrated into the ACT fibers to form an ACT/S nanocomposite. The mass of ACT is  $\sim 2\text{ mg cm}^{-2}$ . The sulfur loading of ACT/S composite was measured to be  $\sim 5.5\text{ mg cm}^{-2}$ .

To prepare ACT/S-rGO nanocomposites, graphene oxide solution with a concentration of  $\sim 4\text{ mg mL}^{-1}$  was prepared using a modified Hummers method [54]. The ACT/S nanocomposite was dipped in the graphene oxide solution. A piece of ACT was also soaked in the same graphene oxide solution to serve as a reference for calculating the loading of graphene oxide in ACT/S-rGO. After drying for 6 h at  $80^\circ\text{C}$ , the as-prepared ACT/S-rGO was heated at  $200^\circ\text{C}$  for 2 h to facilitate the reaction between sulfur and graphene oxide. Such thermal treatment process partially reduced the graphene oxide to conductive reduced graphene oxide. The loading of sulfur was calculated by weighing the ACT/S-rGO and ACT/rGO electrode with the same size. The mass of the ACT/rGO is  $\sim 3\text{ mg cm}^{-2}$ . The sulfur loading of the as-prepared ACT/S-rGO electrode was measured to be  $\sim 4.5\text{ mg cm}^{-2}$ . The mass ratio of sulfur in the ACT/S-rGO composite is  $\sim 60\%$ .

### 2.2. Preparation of Flexible Porous ACT Interlayer

A piece of cotton textile was first soaked with 1 M KOH solution. The KOH loaded textile was then dried at  $80^\circ\text{C}$  for 6 h. The KOH treated textile was thermally treated at  $1000^\circ\text{C}$  for 1 h with an argon flow of 300 sccm. The obtained KOH-activated ACT was further washed using distilled water and then dried in vacuum oven at  $105^\circ\text{C}$  for 24 h. The mass of the porous ACT is  $\sim 1\text{ mg cm}^{-2}$ .

### 2.3. Characterization Methods

Scanning electron microscopy (SEM; FEI Quanta 650) and transmission electron microscopy (TEM; JEOL 2000FX), high resolution transmission electron microscopy (HRTEM, FEI Titan), X-ray diffraction (XRD; PANalytical X'Pert Pro Multi-Purpose Diffractometer (MPD)) equipped with  $\text{Cu K}\alpha$  radiation with  $\lambda = 0.15406\text{ nm}$ , Raman spectroscopy (Renishaw InVia Raman microscope at  $514\text{ nm}$  with 5% laser power), atomic force microscopy (AFM; Dimension Icon with ScanAsyst, Bruker) were used to characterize the structure of the as-prepared samples at different length scales.

### 2.4. Electrochemical Characterization of Flexible ACT/S-rGO Hybrid Cathode

The electrochemical properties of the ACT/S-rGO cathode were measured by using CR2032 type coin cells. The flexible ACT/S-rGO nanocomposite was directly used as the binder-free cathode material without adding any conductive agent. The ACT/S-rGO hybrid textile was punched into circular disks and dried at  $60^\circ\text{C}$  for

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