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# A self-supported carbon nanofiber paper/sulfur anode with high-capacity and high-power for application in Li-ion batteries

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ABSTRACT

A self-supported carbon nanofiber paper (CNFP)/sulfur composite is investigated as the anode of Li-ion batteries instead of the cathode of lithium-sulfur batteries. Relative to the total mass of all the electrode components, the CNFP/sulfur anode exhibits a reversible capacity of ~310 mAh $g^{-1}$. Moreover, the CNFP/sulfur anode maintains 95% of capacity after 1000 cycles and exhibits considerably better high-power capability than the graphite anode. Different from the conventional lithium-sulfur batteries that are based on the conversion reaction of sulfur to $Li_2S$ in the potential range of 3.0–1.5 V vs. Li/$Li^+$, it is assumed that the reversible Li-ion storage ability of sulfur below 1.5 V vs. Li/$Li^+$ in the CNFP matrix can be attributed to the rapid adsorption/desorption of Li-ions on the surface of sulfur. The average working voltage of 3.0 V for a full cell consisting of CNFP/sulfur anode and $LiFePO_4$ cathode demonstrates the successful application of carbon/sulfur anode in Li-ion batteries.

## 1. Introduction

Since the discovery of reversible $Li^+$ intercalation/deintercalation into/from graphite with a low working potential approximating that of Li/$Li^+$, Li-ion batteries (LIBs) were successfully developed by Sony in 1990, and this was a significant breakthrough in the field of electrochemical energy storage and conversion. So far LIBs have dominated the entire electronic appliance market for small and medium scale applications due to their unique advantages over traditional batteries. However, the sluggish $Li^+$ intercalation/deintercalation kinetics and low theoretical capacity (372 mAh $g^{-1}$) of graphite anode make it difficult to achieve a high capacity at high power density. High power is one of the prerequisites for large scale applications of LIBs in electric vehicles (EVs) or hybrid electric vehicles (HEVs). Therefore, research and development (R&D) of alternative high performance anodes beyond graphite are still urgently necessary to meet the high energy and high power demands of LIBs [1–11].

On the basis of the reaction mechanism with Li, other anode materials that are being intensively researched for LIBs application can be mainly classified into three types: intercalation, conversion, and alloy types [3,12]. The most popular intercalation type material is $Li_4Ti_5O_{12}$, which has been practically applied to the consumer market by some corporations due to the improvement in power density. Nonetheless, the use of $Li_4Ti_5O_{12}$ anode sacrifices the energy density of LIBs due to its lower reversible capacity (175 mAh $g^{-1}$) and higher working potential (1.5 V vs. Li/$Li^+$) than graphite anode [13–17]. The conversion type anodes include many transition-metal oxides and sulfides, showing higher capacity and better power capability than insertion type anodes [9,18–25]. However, their wide working potential range (usually 0–3.0 V vs. Li/$Li^+$) makes them almost impossible to be practically used in LIBs. Alloy-based anodes hold greater promise than the other two types because of their high capacity and low working potential that reaches the criterion of commercial market, but they suffer seriously from the large volume variation during charge/discharge [2,26–31]. The attendant cracking and pulverization of electrode components lead to poor cyclability of alloy-based anodes [32]. In summary, to realize the large-scale practical application of LIBs in high-power EVs, R&D of anode materials should follow the main

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principles of (1) low-cost, natural abundance, and easy operation, (2) sufficiently low working potential, (3) high capacity, good power capability and long cycle life.

In this work, we innovatively introduce a carbon/sulfur composite as the anode material of LIBs. Due to the outstanding advantages of sulfur such as abundant resources, cheapness, environmental friendliness, easy recycling, and high theoretical capacity of 1675 mAh $g^{-1}$ upon $Li^+$ uptake, lithium-sulfur batteries are considered as the most promising next-generation high-energy batteries and are intensively studied presently [33–37]. Because of the low electronic conductivity and facile dissolution of the intermediate discharge products of sulfur, the combination of sulfur with porous carbon materials is widely adopted to improve the electrochemical performance of lithium-sulfur batteries [38–41]. Herein, from an unconventional perspective, the carbon/sulfur composite is employed as the anode of LIBs instead of the cathode of lithium-sulfur batteries. In a self-supported carbon nanofiber paper (CNFP)/sulfur anode, sulfur can contribute to a reversible capacity of 637 mAh $g^{-1}$ in the potential range of 1.5–0 V vs. Li/$Li^+$, meeting the high-capacity and low working potential requirements of commercial anodes. Taking the total mass of the whole anode into account, the self-supported CNFP/sulfur anode (conductive agent, binder, and current collector were not used) exhibits a reversible capacity of ~310 mAh $g^{-1}$, which is much higher than a commercial Cu foil-supported graphite anode (80 mAh $g^{-1}$). More importantly, the CNFP/sulfur anode exhibits excellent high-rate behavior, maintaining a reversible capacity of 258 mAh $g^{-1}$ at a current density of 8000 mA $g^{-1}$, in sharp contrast to the poor rate behavior of commercial graphite anode. The capacity retention of 95% after 1000 continuous cycles demonstrates the long-term cycling stability of CNFP/sulfur anode. The full cell composed of CNFP/sulfur anode and $LiFePO_4$ cathode can be cycled reversibly with an average discharge plateau of 3.0 V. These initial results demonstrate the successful application of CNFP/sulfur anode in high-power LIBs.

## 2. Experimental

### 2.1. Preparation of electrospun carbon nanofibers paper

1.5 g of polyacrylonitrile was first dissolved into 15.5 ml of dimethylfuran through vigorous stirring at 60 °C for 6 h. The above solution was electrospun into nanofibers paper at a working voltage of 1–20 kV. The flow rate of the solution and needle tip-to-plate collector distance were fixed at 1 mL $h^{-1}$ and 15 cm, respectively. The as-spun polyacrylonitrile nanofibers paper was heated from room temperature to 250 °C at a heating rate of 1 °C/min and then kept at 250 °C for 1 h in air. At last, the nanofibers were carbonized at 1000 °C for 2 h. The thickness and areal mass of carbon paper is 200 μm and 2.5 mg $cm^{-2}$

### 2.2. Preparation of CNFP/sulfur electrodes

Sulfur was infiltrated into CNFP by spreading a certain amount of sulfur powder onto its surface uniformly, followed by heating at 155 °C under the protection of Ar for 10 h. The content of sulfur in CNFP/sulfur composites was adjusted ranging from 15 wt% to 60 wt %. The self-supported CNFP/sulfur was then cut into small disks, which were used directly as the electrodes to assemble coin-cells.

### 2.3. Electrochemical testing

CR2032-type coin cells were assembled for electrochemical testing. Half-cells were assembled using Li foil as the counter electrode. 1.0 M $LiPF_6$ dissolved in ethyl carbonate/dimethyl carbonate (1/1 v/v ratio) was used as the electrolyte. All the electrolyte components are provided by Shenzhen Capchem Polytron Technologies Inc. After drying at 60 °C under vacuum overnight, the self-supported CNFP/sulfur disks were used as the electrodes to assemble coin-cells. The amount of electrolyte added in each coin-cell is about 0.3 mL. The mass of each carbon nanofiber paper disk is about 3.3 mg. The mass of CNFP/sulfur electrode varies with the sulfur content (from 15 to 60 wt%). The CNFP/sulfur-based half-cells were galvanostatically discharged/charged in the potential range of 2.0–0 V on a Land 2001A charge/discharge tester. For the assembly of graphite-based half-cells, the working electrode was prepared through spreading the slurry of graphite, Super P–Li, and poly (vinylidene fluoride) (PVDF) binder with a weight ratio of 9/0.5/0.5 dispersed in methyl-2-pyrrolidinone onto Cu foil. The $LiFePO_4$ working electrode was prepared by spreading the slurry of $LiFePO_4$, Super P–Li, and PVDF binder with a weight ratio of 8.5/1/0.5 onto Al foil.

## 3. Results and discussion

The morphologies and porous properties of CNFP are shown Fig. S1, S2 and S3. The as-prepared CNFP/sulfur composites containing 15, 30, 45, and 60 wt% of sulfur are denoted as CNFP/S-15, CNFP/S-30, CNFP/S-45, and CNFP/S-60, respectively. The self-supported CNFP/sulfur paper was then cut into small disks (Fig. S4), which were used directly as the electrodes to assemble coin-cells. The assembled half-cells were galvanostatically discharged (lithiation) and charged (delithiation) in the voltage range of 2.0–0 V.

The initial three discharge/charges curves of pristine CNFP electrode are shown in Fig. 1a. During the first discharging, the small potential plateau at about 0.8 V originates from the irreversible reduction decomposition of electrolyte solution [42,43]. The coulombic efficiency of the first cycle is 39%, suggesting a severe decomposition of electrolyte, which can be correlated to the highly porous and active surface of CNFP. The reversible (charge) capacity of CNFP in the third cycle is 170 mAh $g^{-1}$, after which the capacity stays almost constant, suggesting its excellent cycling stability as the matrix of sulfur anode (Fig. S5).

The discharge/charge curves of CNFP/sulfur electrodes with different sulfur loadings are shown in Fig. 1b–e. When sulfur accounts for 15 and 30 wt% of electrode mass, the shapes of the discharge/charge curves are similar to those of pristine CNFP. During the first discharge, the short plateaus representative of the reduction decomposition of electrolyte are located at about 0.9 V, which is slightly higher than that with pristine CNFP electrode. This phenomenon may be related to the presence of sulfur influencing the reduction potential of electrolyte. Relative to the total mass of the electrode (including both CNFP and sulfur), the reversible capacities of CNFP/S-15 and CNFP/S-30 electrodes in the third cycle are 225 and 310 mAh $g^{-1}$, respectively, which are considerably higher than those of pristine CNFP electrode (170 mAh $g^{-1}$). It is very interesting to note that the typical discharge plateaus at around 2.3 and 1.9 V corresponding to the conversion reaction of sulfur to $Li_2S$ in lithium-sulfur batteries [37,44] are not observed in the present systems. However, the significantly improved capacity of CNFP-based electrodes upon incorporation of 15 and 30 wt% sulfur indeed reflects the electrochemical activity of sulfur for Li-storage in the potential range of 2.0–0 V vs. Li/$Li^+$. Furthermore, the high coulombic efficiency (94–100%) of CNFP/S-15 and CNFP/S-30 electrodes after the initial discharge/charge indicates good reversibility of sulfur for Li-ion storage in this working potential range. These discharge/charge behaviors suggest that the electrochemical Li-ion storage mechanism of sulfur in the present systems is different from that in conventional lithium-sulfur batteries, and