



A freestanding hollow carbon nanofiber/reduced graphene oxide interlayer for high-performance lithium–sulfur batteries



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ABSTRACT

Rechargeable lithium–sulfur (Li–S) batteries have attracted more and more attention in recent years, and a large number of efforts have been made to improve their electrochemical performance. Herein, a freestanding hollow carbon nanofiber/reduced graphene oxide (HCNF/rGO) interlayer is prepared by simple method via vacuum filtration and heat treatment. The utilization of the HCNF/rGO interlayer enables the inhibition of the diffusion of polysulfides and offers unobstructed channels for ions and electrons. An initial specific discharge capacity of 1318.4 mAh g⁻¹ at 0.2 C and a capacity fade of 0.13% per cycle at 1 C of Li–S cells with the HCNF/rGO interlayer are achieved. Meanwhile, the cells exhibit outstanding rate capability with a discharge capacity of 630 mAh g⁻¹ at a discharge current density of 10 C. Therefore, a HCNF/rGO interlayer with specific structure demonstrates potential for high-performance Li–S batteries.

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1. Introduction

With the increasing development of electrical vehicles and large-scale smart grids, Lithium-ion batteries (LIBs) with traditional cathode materials are not sufficient to meet the demand for high energy density [1,2]. In recent years, lithium–sulfur (Li–S) batteries are regarded as an attractive alternative on account of their high theoretical capacity of 1675 mAh g⁻¹ and energy density of 2600 Wh kg⁻¹ [3–6]. In addition, Li–S batteries are attractive owing to abundant resource, environmental friendliness and low cost, which make them more suitable for commercialization [7–9]. However, the low electronic/ionic conductivity of sulfur and the discharge products, large volume change of sulfur during the lithiation/delithiation processes, and the shuttling of dissolved lithium polysulfides (Li₂S_x, 4 ≤ x ≤ 8) in organic liquid electrolytes during cycling significantly hampered the practical applications of Li–S batteries. These problems eventually lead to the low electrochemical utilization of sulfur, poor cycling stability and rate capability [10–15].

To address these issues of Li–S batteries, especially shuttle effect, conductive porous frameworks such as carbon materials

[16–18], conducting polymers [19,20], and metal oxides [21,22] have been employed. It has been confirmed that the introduction of conductive porous frameworks can not only restrict sulfur with high electronic conductivity and enough space for volume expansion but also suppress the diffusion of polysulfides. Nevertheless, the fabrication procedures are always complicated and the active materials loading in the cathode gets decreased [23–25].

As an important component in battery systems, the separator serves as an electronic insulator and ionic conductor, through which electrolyte can diffuse freely between the cathode and anode [26]. What's more, polysulfides generated in Li–S batteries can also diffuse through the separator and react with the metal lithium anode, resulting in the degradation of the performance of batteries. An alternative approach to restrain the shuttle effect and improve the utilization of active material is to insert a conductive and porous carbon interlayer between the cathode and the separator. Manthiram and coworkers have proposed a few interlayers composed of multi-walled carbon nanotubes (MWCNTs) [27], carbon nanofiber (CNF) [28] and treated carbon paper [29]. In addition, graphene oxide (GO) [30], bacterial cellulose (BC) derived nanofibers [31] and polypyrrole nanotube film [32] have also been raised to act as an interlayer for Li–S batteries. The carbon interlayer approach involves simple fabrication procedures and an interlayer can serve as a upper-current collector, effectively reduce charge-transfer resistance and localize the soluble polysulfides during cycling, thus offering a simple and effective solution to fabricate

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Li–S batteries with excellent electrochemical performance.

Herein, a hollow carbon nanofiber/reduced graphene oxide (HCNF/rGO) slice (about 50 μm and 1.2 mg cm^{-2}) is raised to act as an effective interlayer between the cathode and the separator. The rGO is introduced to the HCNFs, constructing a 3D conductive framework and physical barriers to physically constrain polysulfides. Electrochemical results exhibit an initial discharge capacity of 1318.4 mAh g^{-1} at 0.2 C and a capacity fade of 0.13% per cycle at 1 C. Meanwhile, the cells with the HCNF/rGO interlayer exhibit outstanding rate capability with a discharge capacity of 630 mAh g^{-1} at a discharge current density of 10 C.

2. Experiment details

2.1. Materials preparation

HCNFs were purchased from Sigma–Aldrich, and were soaked with concentrated nitric acid (HNO_3) and sulfuric acid (H_2SO_4) (1:3, by volume) at room temperature for 12 h before used. Graphite oxide (GO) was synthesized from natural graphite powders by using the modified Hummers method [33]. Subsequently, 15 mg HCNFs and 5 mg GO were dispersed in 100 mL distilled water by ultrasonication for 30 min and magnetic stirring for another 30 min. Then, the suspension was filtered by vacuum filtration. After heated at 800 $^\circ\text{C}$ under Ar atmosphere for 2 h, a flexible HCNF/rGO layer was obtained.

2.2. Material characterization

The morphology of the samples was investigated by field emission scanning electron microscopy (SEM, Nova Nano SEM 230). The elements on the surface of sample were identified by energy-dispersive X-ray spectroscopy (EDS).

2.3. Electrochemical measurements

The S cathode was fabricated by a slurry coating method. The composite cathode slurry was composed of precipitated sulfur (Sigma–Aldrich, 100 mesh particle size powder), acetylene black and polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidone (NMP) at the weight ratio of 6: 3: 1. The slurry of the cathode was coated onto an aluminum foil with a doctor blade, dried under vacuum at 60 $^\circ\text{C}$ for 12 h. Then the cathode was cut into pellets with a diameter of 1.0 cm and the active sulfur loading was about 1.4 mg cm^{-2} . CR2025-type coin cells were assembled in an argon-filled glove box to avoid contamination by moisture and oxygen. The electrolyte was made up of 1 M bis(trifluoromethane) sulfonamide lithium salt (LiTFSI, Sigma Aldrich) dissolved in a mixture of 1,3-dioxolane (DOL, Acros Organics) and 1,2-dimethoxyethane (DME, Acros Organics) (1: 1, by volume), with 0.1 M LiNO_3 as an electrolyte additive. Lithium wafer was used as counter electrode and a HCNF/rGO interlayer was put between the cathode and a celgard 2400 separator. A 1470e electrochemical measurement system was applied to measure cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV tests were performed at a scan rate of 0.2 mV s^{-1} with a voltage range of 1.8 V–2.8 V. EIS measurements were carried out at open-circuit potential (OCP) in the frequency range between 100 kHz and 10 mHz with a perturbation amplitude of 5 mV. Galvanostatic charging–discharging tests were performed in the voltage range of 1.8 V–2.8 V at 25 $^\circ\text{C}$ by using a LAND CT2001A battery-testing instrument.

3. Results and discussion

Fig. 1a illustrates the fabrication of the HCNF/rGO interlayer, implying the HCNF/rGO interlayer can be easily obtained without complex fabrication procedure. As shown in Fig. 1b, when a HCNF/rGO interlayer is applied as a barrier in Li–S cell between the cathode and the separator, the polysulfides are expected to be confined in the cathode region, thus the shuttle effect can be significantly suppressed. Fig. 1c shows the HCNF/rGO interlayer has good mechanical strength, so that Li–S cells can keep robust stability during its assembly and cycles.

Fig. 2a shows charging–discharging curves at 0.2 C of the Li–S cells with and without the HCNF/rGO interlayer. The two remarkable reduction peaks at about 2.31 V and 1.99 V correspond to the first reduction from S_8 to long-chain polysulfides (Li_2S_x , $4 \leq x \leq 8$) and the second reduction from long-chain polysulfides to short-chain $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, respectively [34]. The second reduction is a slower kinetic process than the first one and accounts for a larger proportion of the capacity [35]. Two oxidation peaks at 2.35 V and 2.44 V are observed, suggesting the transformation of Li_2S into high-order polysulfides and eventually to sulfur.

The CV curves at 0.2 mV s^{-1} of Li–S cells with a HCNF/rGO interlayer are shown in Fig. 2b. The two reduction and oxidation peaks are consistent with the two discharge and charge plateaus shown in the charging–discharging curves. For the cells with and without the HCNF/rGO interlayer, the initial discharge capacities are 1318.4 and 971.3 mAh g^{-1} . The higher discharge capacity suggests higher sulfur utilization, indicating the insert of a HCNF/rGO interlayer can make better contact of electrolyte and cathode and involve more active material into reaction. In comparison, the cells with the HCNF/rGO interlayer exhibit higher discharge capacity and discharge plateaus, indicating better electrochemical reversibility [36–38].

Rate capability of the cells with and without the HCNF/rGO interlayer is carried out at various rates from 0.2 to 10 C, as shown in Fig. 3a. When the current rate increased to 2, 5 and 10 C, the cells with the HCNF/rGO interlayer deliver a higher capacity of 805, 739, 630 mAh g^{-1} , respectively. After cycling at various rates, when the current rate is back to 0.5 C, a stable capacity of over 800 mAh g^{-1} is obtained. The outstanding rate capability accounts for the good electrolyte infiltration and excellent ionic and electronic conductivity of the interlayer. The cycling performance shown in Fig. 3b reveals that cells with the HCNF/rGO interlayer exhibit excellent cycle stability and high sulfur utilization. After 100 cycles, the discharge capacities of the cells are 779.1, 715.8 and 690.4 mAh g^{-1} at 1 C, 2 C and 5 C rates. The excellent cycle stability at various rates arises from the soluble polysulfides are well absorbed in the cathode and the insoluble discharge products $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ can participate in the reaction again. Meanwhile, the cells with the HCNF/rGO interlayer exhibit relatively cycle stability at high current density, indicating that the HCNF/rGO has excellent ionic and electronic conductivity. Therefore, Li–S cells with the HCNF/rGO interlayer show excellent rate capability and relatively cycle stability at high current density.

As illustrated in Fig. 4, a long-term cycling test is also conducted for the cells with and without the HCNF/rGO interlayer, of which the final discharge capacities are, respectively, 533.6 and 214.2 mAh g^{-1} . Thus, the corresponding capacity fade of per cycle is 0.13% and 0.18% after 400 cycles at a current density of 1 C. Besides, the coulombic efficiency of cells with the HCNF/rGO interlayer remains higher than the traditional Li–S cells, indicating a better alleviation of the shuttle effect. In addition, there is significant decline of the first 20 cycles, which can be mainly ascribed to the poor electronic conductivity of sulfur, the shuttle effect and the volume expansion of the cathode. Therefore, a HCNF/rGO interlayer

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