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Lithium–sulfur batteries with superior cycle stability by employing porous current collectors

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A B S T R A C T

Conventional lithium–sulfur (Li–S) batteries suffer from severe capacity fade and self-discharge attributed to sulfur dissolution and polysulfide diffusion. Here we present a porous cathode architecture which suppresses the loss of active material and self-discharge behavior in Li–S systems. 3D sulfur–nickel foam cathodes (SNF cathodes) have porous, electrically conductive Ni foam substrates as bifunctional current collectors. It was found that these cathodes have a stable cycle life with a high discharge capacity retention rate of 92% after 50 cycles. Moreover, the SNF cathodes reduce the self-discharge and retain 85% of their original capacities after resting for two months. The porous architecture of Ni foam accommodates the active material and traps polysulfides in the cathode region during cycling and battery storage, effectively reducing the loss of active material and capacity. In addition, it provides an excellent internal electron transport network by ensuring intimate contact between the active material and Ni foam, resulting in low internal impedance and improved capacities. The study demonstrates that the 3D Ni foam is an attractive bifunctional current collector for Li–S batteries.

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1. Introduction

Rechargeable batteries with a stable cycle life and a high specific capacity are a key to meeting the ever-increasing requirements of global energy storage market, such as portable electrical devices, electric vehicles, and storage systems for renewable energy. Traditional metal oxide cathodes, such as $LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$, have limited practical capacities of less than 200 mAh g^{-1}. The continued use of transition-metal oxides as cathodes further raises the problems of cost, toxicity, and environmental concern [1,2]. Thus, development of alternative cathode materials is critical for next generation rechargeable batteries.

Li–S batteries, employing sulfur as the cathode and metallic lithium as the anode, are increasingly being investigated due to their high theoretical capacity [1–3]. In contrast to the traditional metal oxide cathodes, which undergo lithium insertion/extraction into/from a host structure, sulfur cathodes undergo an electrochemical conversion reaction, providing a theoretical capacity of 1675 mAh g^{-1} and energy density of 2600 Wh kg^{-1} with an average operating voltage of ∼ 2.1 V [1–3]. Additionally, sulfur offers significant other benefits of low cost, environmental benignity, and natural abundance [3,4]. However, several obstacles must be overcome to facilitate the commercialization of Li–S batteries: lower practical capacity, poor cyclability and severe self-discharge. First,

the specific capacity of Li–S batteries is limited by the insulating nature of sulfur and its final discharge products, Li_2S_2 and Li_2S [2,4]. Second, the poor cyclability is due to the high solubility of the intermediate polysulfides, Li_2S_x ($2 < x \leq 8$), in the liquid electrolyte during the charge/discharge process, leading to an irreversible loss of the active material and capacity [4–6]. The dissolved lithium polysulfides easily diffuse through the separator and shuttle between the anode and cathode. In the anode region, the polysulfides can corrode the metallic Li anode [2]. In the cathode region, the polysulfides are converted into Li_2S/Li_2S_2 forming an insulating precipitation on the cathode surface [5,6]. These phenomena result in severe capacity fade and a short cycle life. Third, the sulfur dissolution and polysulfide shuttle effect during battery storage result in short shelf-life of the cells [7–9].

To overcome the above challenges and develop high-performance Li–S batteries, current efforts are focused on (i) improving the electrical conductivity of sulfur cathodes and (ii) accommodating or absorbing the active material and lithium polysulfides in the cathode region. For example, conductive additives, such as various carbon materials [10–13] or conducting polymers, have been used in sulfur cathodes [14–17]. A number of researchers have successfully synthesized porous composites [18–20] or inserted a free-standing interlayer into the cathodes [21,22] to enhance the cycling stability of the cells. Many porous carbon templates or free-standing carbon papers have been used to accommodate or adsorb dissolved lithium polysulfides in the cathode region by providing abundant pore spaces [18–22]. However, very few studies have explored the architecture of metal current

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collectors. Thus far, the design of alternative current collectors has included the Ni-coated 3D steel sheet [23], micro-network Ni substrate [24,25], and Ni foam matrix with various morphologies [26–29]. The 3D metal sheet, porous metal foam, and metal fiber matrix have been applied in nickel/metal hydride batteries [23–26] and in LiFePO$_4$-based lithium-ion batteries [27,28]. Bare and rigid Ni foam combined with the polysulfide-based electrolyte systems has been used to improve the cycling performance of Li–S batteries [29,30].

We investigate here the feasibility of 3D sulfur–nickel foam (SNF) cathodes by applying Ni foam matrices as a bifunctional current collector in Li–S batteries. In the SNF cathodes, the Ni foam matrix works as an electron transport network to improve the electrical conductivity of the cathode, as a container to accommodate the active material, and as a cage to retain the polysulfides in the cathode region during the charge/discharge process. The SNF cathodes are prepared by a facile paste-absorption method to optimize the porous structure of the cathode by improving the contact between the active material and the foam matrix. We find that Li–S batteries employing SNF cathodes exhibit superior cycle stability, high discharge capacity, excellent capacity retention, and low self-discharge behavior.

2. Experimental

2.1. Paste-absorption method for 3D SNF cathode fabrication

Pristine sulfur used in the SNF cathodes was synthesized by a precipitation method at room temperature [31–33]. The pristine sulfur was mixed with carbon black (Super P) and polyvinylidene fluoride (PVDF, Kureha) in the weight ratio of 60:30:10 and 70:20:10, and was then dispersed in N-methyl-2-pyrolidone (NMP). The pastes were vigorously stirred for 24 h to ensure a homogeneous mixture. The viscous and well-mixed paste was then loaded into the Ni foam, which has a thickness of 0.14 mm and a diameter of 12 mm.

The paste-absorption method for porous cathode fabrication is illustrated in Fig. 1. First, the well-mixed paste was dropped onto a petri dish. Each paste drop was covered by a Ni foam disk and allowed to absorb for 2 min by the capillary force. Second, the Ni

foam substrates were pressed to channel the absorbed paste into the inner pore spaces of the Ni foam, and to ensure a uniform sulfur coating on the skeleton of the Ni foam. Then, the SNF cathodes were dried in a convection oven at 50 °C for 24 h. The dried SNF cathodes were then roll-pressed from the thickness of 0.14 to 0.1 mm. The resultant 3D SNF cathodes were uniformly loaded with the same amount of active material (2.0 mg cm^{-2} sulfur) and had a close connection between the active material and the metal substrate.

2.2. Cell assembly

The prepared SNF cathodes were dried in a vacuum oven at 50 °C for 2 h before assembling the cell. SNF cathodes, polypropylene separators (Celgard), lithium foil anode and nickel foam spacers were placed in a sequence into CR2032 coin-type cells with an electrolyte of 1.85 M LiCF$_3$SO$_3$ salt (Acros Organics) in a 1:1 volume ratio of 1,2-dimethoxyethane (DME; Acros Organics) and 1,3-dioxolane (DOL; Acros Organics). The coin cell assembly was conducted in an argon-filled glove box.

We also compared the cells with conventional cathodes that were prepared by the slurry casting method on flat aluminum foils as current collectors. The same coin cell assembly process was followed as described above. These two kinds of cathodes were controlled with the same compositions and mass of the active material.

2.3. Electrochemical measurements and microstructure characterizations

The cyclability tests were performed with a computer-controlled Arbin battery cycler at room temperature. After assembling, the cells were allowed to rest for 30 min at 25 °C, then discharged to 1.5 V, and charged to 2.8 V. The self-discharge behavior of the cells was investigated by measuring the first discharge capacity and the open-circuit voltage (OCV) of the cells with different resting times. Cyclic voltammetry (CV) measurement was applied to the SNF cathodes using a VoltaLab PGZ 402 Potentiostat. The voltammogram was recorded at a scan rate of 0.1 mV s^{-1}, with a potential range between 2.8 and 1.5 V. The electrochemical impedance spectra (EIS) of the cells were recorded with a Solartron SI 1260/SI 1287 impedance analyzer between 1 MHz and 0.1 Hz and
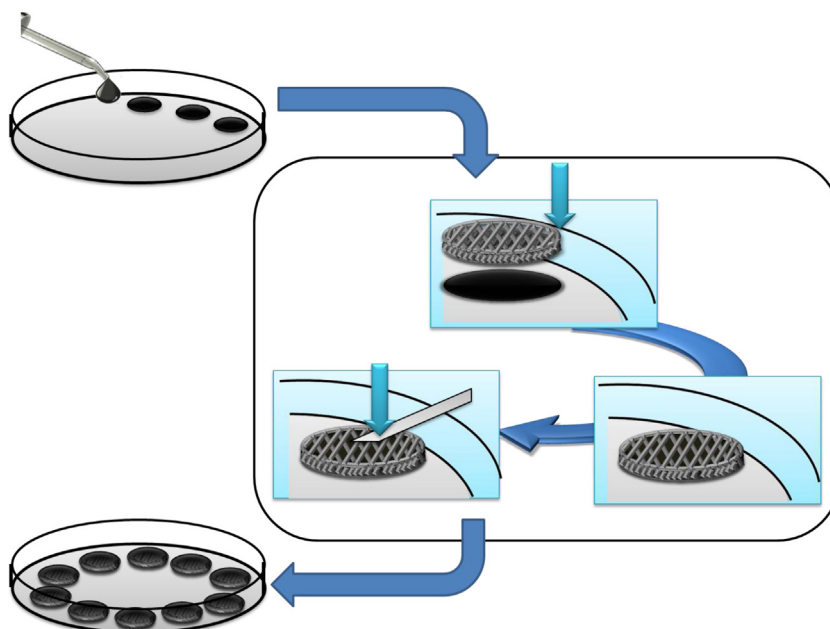

Fig. 1. Illustration of the paste-absorption method for the 3D SNF cathode fabrication.