Chemical Engineering Journal 350 (2018) 411–418

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

N-doped foam flame retardant polystyrene derived porous carbon as an efficient scaffold for lithium-selenium battery with long-term cycling performance

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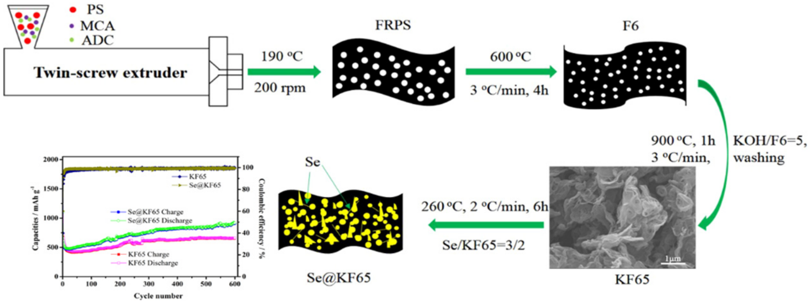
HIGHLIGHTS

- Hierachically porous carbon has been fabricated by foamed polymer.
- After selenization, Se was implanted into the hierachically porous carbon.
- The as-prepared composite exhibited excellent rate capability and cycle stability.
- The capacity was up to 917.8 mAh g^{-1} at 1 A g^{-1} after 600 cycles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
N-doped
Foam
Polystyrene
Nanostructures
Porous carbon

ABSTRACT

Owing to the preponderances in easy preparation and low cost, N-doped foam flame retardant polystyrene (FRPS) could be regarded as a sustainable precursor to develop porous carbonaceous frameworks for the encapsulation of elemental selenium. In this paper, an electrode material of Se encapsulated in N-doped foam flame retardant polystyrene based porous carbon framework (Se@KF65) was fabricated by carbonization/activation of N-doped foam polystyrene and selenium-loading for high-performance lithium batteries. Due to the fact that KF65 acted as a stable matrix for Se and facilitates electronic conductivity and ion transportation, the Se@KF65 composite exhibited large reversible capacity, high rate performance and durable long-term cycling stability. Moreover, the high specific surface area, large pore volume and good electron conductivity of Se@KF65 composite showed the reversible electrochemical reaction of selenium towards metallic Li, and at the current density of 1 A g^{-1}, Se@KF65 composite electrode exhibited a reversible capacity of 917.8 mAh g^{-1} after 600 cycles. The easily obtained mi/macrospores features of Se@KF65 composite indicated that large-scale treatment of the polymer material may find its potential application in renewable green energy storage.

1. Introduction

Lithium-ion batteries (LIBs) with high energy storage capacity, excellent stability and environmental friendliness have been widely regarded as a promising power source for portable electronic devices in recent years [1–3]. Carbonaceous materials with different

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https://doi.org/10.1016/j.cej.2018.06.010
Received 14 April 2018; Received in revised form 31 May 2018; Accepted 3 June 2018
Available online 04 June 2018

morphologies and structures have been widely used in the study of LIBs electrode materials [4–8]. In order to improve the energy storage capacity of carbonaceous materials, plenty of amorphous carbon materials with porous structure have been investigated [9–12]. Due to that porous carbon can effectively improve the reversible storage capacity and shorten the diffusion distance of lithium ion, porous carbonaceous materials have higher storage capacity of lithium ion than other traditional materials [13–15]. In addition, the high cost of current lithium ion battery electrode materials are also an issue that needs to be solved urgently.

Owing to their high molecular weight, low density, excellent performance, rich sources of raw materials and easy preparation, polymer materials have now been applied to all aspects of life. Polystyrene, with a general structure of "the head and tail", is constructed by a main saturated carbon chain and the side conjugated benzene ring, which can increase the rigidity of the molecule to avoid material collapse. The most important feature of polystyrene is its excellent thermal stability and fluidity when melted, so it is easy to form and process in large scale. Meanwhile, the cost of polystyrene is much lower than other carbonaceous materials, such as CMK-3 [16]. Nitrogen-containing flame retardants are mainly melamine (including its derivatives) and related heterocyclic compounds, which can maintain a certain structure of materials (such as: polystyrene) at high temperature. Also, because of the existing of N element, N-doped flame retardants will increase electrochemical performance of the material [17]. Foaming agents, by means of decomposing into gases such as carbon dioxide and nitrogen at comparatively high temperature, can develop fine pores in a target polymer composite [18]. Foaming process can not only increase the content of macropores in the materials, but also form mesopores and micropores, which are beneficial for the improvement of specific surface area and battery performance.

Lithium-sulfur (Li-S) battery, due to its high theoretical capacity (1672 $\mathrm{mAh\,g^{-1}}$) and superior energy density (2600 $\mathrm{Wh\,kg^{-1}}$), is considered to be a promising next-generation rechargeable battery [19–22]. Besides, sulfur, which is cheap, abundant and environmentally friendly [23]. However, the practical application of Li-S battery has been hampered by two major issues [24–26]: (1) the low electronic conductivity of sulfur ($5.0 \times 10^{-30}\ \mathrm{S\,cm^{-1}}$ at 25 °C) results in poor electrochemical accessibility and low utilization of the sulfur in the electrode; (2) the electrolyte-soluble polysulfide intermediate products formed during the charge/discharge process can be dissolved in the liquid electrolyte, which causes the well-known shuttle effect and leads to the rapid loss of capacity. In recent years, many efforts have been made to explore new electrode materials to solve these problems [27,28]. Selenium, because of its similar chemical properties to sulfur, good electrical conductivity ($1.0 \times 10^{-3}\ \mathrm{S\,m^{-1}}$) and high (3253 $\mathrm{Ah\,L^{-1}}$) volume capacity, was considered to be one of the most promising electrode materials in Lithium-ion batteries [29–31]. However, due to the dissolution of high order selenium compounds, Se electrode also faces poor cycle performance and low Coulombic efficiency (CE). Recently, plenty of works have been devoted to solving these problems of Li-Se batteries. Combining mesoporous carbon with Se has been proved to be one of the most effective ways to improve the utilization ratio of selenium and to alleviate the shuttle effects of polyselenization [32–34].

In this paper, a simple and effective method was proposed to prepare an electrode material for Li-Se batteries, see Fig. 1. First, the cheap and abundant polymer material (polystyrene) was carbonized. Second, powdered selenium and the pre-carbonized precursor were selenized in accordance with the relevant proportion about 3:2. Herein, the resulting KF65, denoted according to the KOH:F6 (F6 was the pre-carbonized precursor) mass ratio of 5:1, could acquire a high specific surface area of 1888 $\mathrm{m^2\,g^{-1}}$. Furthermore, the relationships between the intrinsic characteristics of the Se@KF65 composite and the electrochemical performances have also been investigated and discussed in detail. When utilized as an electrode material for Li-Se batteries, the composite exhibited large reversible capacity, high rate performance, and long-term cycling stability, which demonstrated a promising way to produce large-scale polymer material for energy-storage system of LIBs.

2. Experimental section

2.1. Materials

Polystyrene (PS) was TOTAL Polystyrene Crystal 1070 provided by Total Petrochemicals (Foshan) Ltd. Nitrogen-containing flame retardant was MELANIC MC (MCA) provided by Nantong Italmatch Chemicals Co., Ltd. Foaming agent (Azodicarbonamide, ADC) was supplied by Ningxia Risheng Industrial Co., Ltd. Solid state KOH, aqueous HCl and powdered selenium (200 mesh) were of analytical grade and were used as purchased. Ultrapure water (18.2 MΩ cm) was used for solution preparation and sample rinse.

2.2. Preparation of the blends

The PS powder was treated at 80 °C for 4 h before processing in order to avoid possible moisture-degradation reactions. Then the PS was melt blended with MCA (5 wt%) and ADC (3 wt%) using a Brabender counter-rotating twin-screw extruder (Germany) with a screw diameter of 25 mm and a length/diameter ratio of 20:1. The temperature profile was 105, 185, 190, 190, 190, 190, 195, 205 °C, and the screw speed was 200 rpm. All the extrudated rods were immediately cooled in a water bath, pelletized and then dried at 80 °C for 4 h. The resulting blends were marked as FRPS.

2.3. Preparation of the samples

Firstly, FRPS was pre-carbonized at 600 °C with a heating rate of 3 $\mathrm{°C\,min^{-1}}$ for 4 h under nitrogen atmosphere. Then, the pre-carbonized precursor (F6) was mixed with KOH at a KOH/F6 weight ratio of 5:1 (or 3:1, 1:1) by physical blending in a mortar, and heated in a 130 °C oven for 2 h to remove moisture. The resulting mixture was then heated to 900 °C at a heating rate of 3 $\mathrm{°C\,min^{-1}}$ and maintained at the target temperature for 1 h under nitrogen atmosphere. Finally, the products (abbreviated as KF65, KF63 and KF61 according to the weight ratio of KOH/F6) were collected by washing with 2 M HCl and deionized water, filtering, and drying at 100 °C. A melt-diffusion method was used to prepare Se@KF65 (or Se@KF63, Se@KF61) composite based on KF65: (i) Se powder and KF65 were ground in an agate mortar at a fixed Se:KF65 weight ratio of 3:2; (ii) subsequently, the ground mixtures were transferred into a porcelain crucible and heat-treated at 260 °C for 6 h with a heating rate of 2 $\mathrm{°C\,min^{-1}}$ under N_2 atmosphere (flow rate: 0.10 $\mathrm{L\,min^{-1}}$).

2.4. Material characterization

The powder X-ray diffraction (XRD) patterns of all samples were recorded on an X-ray diffractometer (D8 Advance of Bruker, Germany) with filtered Cu Kα radiation over the 2θ range of 5–80°. Field emission scanning electron microscopy (FE-SEM) images were collected on a JSM-7800F scanning electron microscope. Transmission electron microscopy (TEM) images were taken on a JEM-2100 transmission electron microscope using an accelerating voltage of 200 kV. High-resolution transmission electron microscope (HRTEM) (JEOL-2011) was operated at an acceleration voltage of 200 kV. The specific surface area was evaluated at 77 K (Quantachrome NOVA1200e) using the Brunauer-Emmett-Teller (BET) method, while the pore volume and pore size were calculated according to the Barrett-Joyner-Halenda (BJH) formula applied to the adsorption branch. Thermogravimetric analysis (TGA) was carried out using a STA409PC from 30 °C to 950 °C at a heating rate of 10 $\mathrm{°C\,min^{-1}}$ under N_2 atmosphere. Element analysis was performed by an Inductively Coupled Plasma-Atomic Emission