



Hierarchically porous carbon derived from waste acrylic fibers for super-high capacity lithium ion battery anodes

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HIGHLIGHTS

- Acrylic fibrous waste has been used to synthesis porous carbon for LIBs anode.
- The carbon derived from waste acrylic have 3D hierarchical porous structure.
- The N-doped porous carbon exhibit excellent electrochemical performances.

ARTICLE INFO

Keywords:

Waste acrylic fibers
Lithium ion batteries anode
Nitrogen-doping
Carbon materials

ABSTRACT

Acrylic fiber is one of three important synthetic fibers in the world. The disposal and reuse of large number of waste acrylic fibers from fabric manufacturers or waste recovery is an urgent economic and environmental issue. Here, a porous carbon was derived from waste acrylic fibers via pre-oxidized, carbonization and KOH activation. Furthermore, we adopted melamine as nitrogen source to dope the porous carbon materials. When used as the anode of lithium ion batteries, this nitrogen-doped porous carbon shows high reversible capacity of ca. 1200 mA h g⁻¹ after 50 cycles at 0.1 A g⁻¹. Reversible capacities of 550 and 370 mA h g⁻¹ are obtained at higher current densities of 1 and 5 A g⁻¹ after 500 cycles, respectively. The outstanding electrochemical performance are a result of its large mesopore volume, high-level N-doping (especially, pyridinic-N), large quantity of edge defects, and three-dimensional hierarchical porous architecture. This paper demonstrates that the reuse of waste industrial acrylic fibers as energy storage materials is a promising method for both energy and environmental fields.

1. Introduction

The issues of rapid energy depletion and severe environmental concerns have attracted more and more attention in recent years. Researchers around the world are struggling to develop renewable energy and reduce the environmental pollution at the same time [1]. Rechargeable lithium ion batteries (LIBs) have been counted as one of the most promising renewable energy storage devices for electric vehicles, portable devices, and renewable energy integration [2–6]. Graphite has been commonly used as commercial anode material due to its high Coulombic efficiency, stability, and safety. However, it encounters some disadvantages such as low theoretical specific capacity (372 mA h g⁻¹), poor rate capability and low safety [7–10]. Intensive efforts have been made to develop alternatives of graphite for next-

generation LIBs with low cost, high energy density, and good cycling performance [11–13]. Due to its high reversible lithium storage capacity and fast lithium storage kinetics, the hierarchical porous carbon has been widely investigated for the fabrication of high-performance electrodes [14,15]. Among these carbon materials, the high lithiation capability and excellent cycling stability could profit from the hierarchical porous structure, which can not only shorten the transport length for Li⁺ ions but also offer large electrode/electrolyte interface for the charge-transfer reaction [16,17]. In addition, the presence of heteroatoms (such as N, B, S, and P) at the carbon surface can enhance its reactivity and provide extra Li⁺ ion storage sites [18,19]. Among the heteroatom, N-doped are attractive due to their electronegativity (3.5) is higher than that of carbon (3.0) [20]. Melamine, with a high N content (66.7 wt%), has been widely used as a N-doped precursor for

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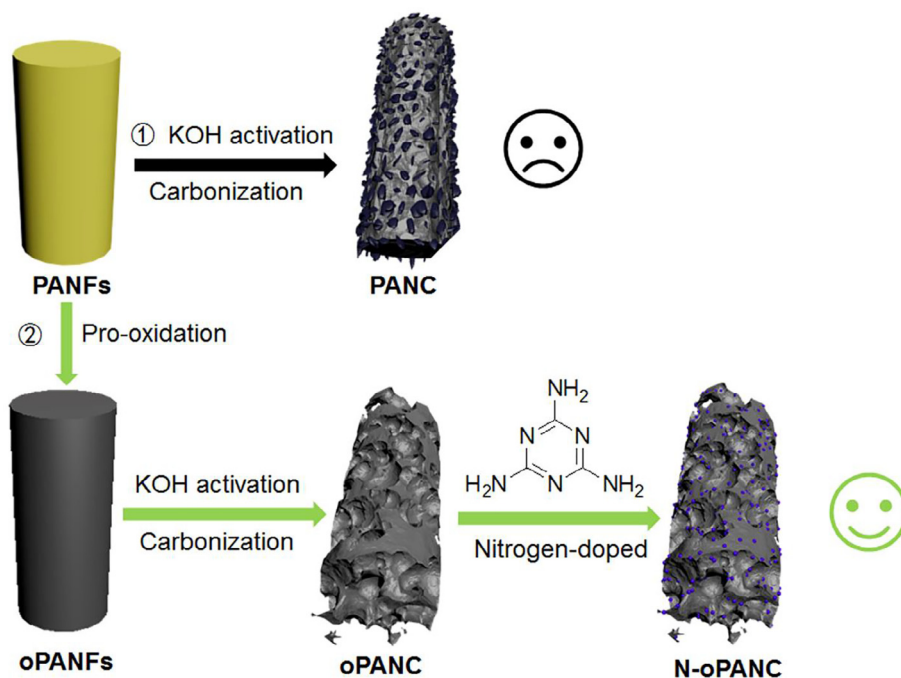


Fig. 1. Schematic illustration of the preparation process of PANC, oPANC, and N-oPANC.

carbon materials [3,21,22].

Acrylic fibers are composed by synthetic polymer originating from fossil energy. Moreover, the acrylic fibers occupy the third largest market share in the global fibers market and their output is over million tons each year [23,24]. Due to the non-biodegradability of synthetic fibers, the disposal of waste acrylic fibers from fabric manufacturers or waste recovery is difficult and becoming an urgent environmental issue [25]. In previous reports, acrylic fibrous waste has been used to synthesis activated carbon via pyrolysis and physical activation with steam [26,27]. Due to its high carbon and nitrogen content, low cost, and virtually dust-free nature [28], the acrylic fibrous waste would be suitable for LIBs anode precursor materials, which is beneficial to both energy and environmental fields.

In present study, we attempted to reuse industrial waste acrylic fibers for LIBs anode via simultaneous carbonization and KOH activation, which is a most efficiency ways to form porous structure [29]. The pre-oxidized technology was introduced before KOH activation to promote the formation of hierarchical porous architecture. In addition, we also adopted melamine as nitrogen source to dope the porous carbon materials. The results revealed that N-doped oPAN-based carbon electrodes show high reversible capacity, excellent cycle performance, and good rate capability. The electrochemical performance of PAN-based carbons has been investigated in detail.

2. Experimental

2.1. Materials

Industrial by-product waste acrylic fibers were obtained from HaoShi Carbon Fiber Co., Ltd., Lanzhou, China. Analytical grade KOH was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., Beijing, China. Melamine (analytical grade) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China. N, N-dimethylformamide (analytical grade, DMF) was obtained from Shanghai Macklin Biochemical Co., Ltd., Shanghai, China. The chemicals were used without further purification.

2.2. Preparation of PANC, oPANC and N-oPANC

The pretreatment of PANFs was as follows: Firstly, a certain amount of PANFs were dispersed into absolute ethanol and stirred violently for about 3 h. Then, they were washed with acetone for 4 h to remove the impurities. Finally, the PANFs were filtered, washed with DI water and dried at 80 °C overnight.

In a typical preparation of the activated PAN-based carbon (PANC), PANFs were mixed with KOH in a small amount of water at a weight ratio of KOH to PANFs equal to 4 in a beaker. After soaking in KOH solution, the mixtures were dried in an oven at 130 °C for 24 h. Next, the mixtures were heated to 800 °C at the heating rate of 2 °C/min in horizontal furnace under nitrogen gas flow (80 ml/min) and held at this temperature for 2 h. Then the activated samples were thoroughly washed with distilled water several times, until neutral pH was achieved. Finally, the PANC was dried in a vacuum oven at 70 °C for 12 h. The PANFs were pre-oxidized at 280 °C in oxygen for 2 h with a heating rate of 5 °C/min and the products were noted as oPANFs. The preparation of activated oPAN-based carbon (oPANC) was similar to the process of PANC. The preparation of the nitrogen-doped activated oPAN-based carbon (N-oPANC) can be conducted as follows: 200 mg oPANC was dispersed in 20 g DMF using ultrasound for 20 min, then 400 mg melamine monomer was added into the solution with stirring. The oPANC/melamine mixture solution was vacuum-filtrated and vacuum-dried at 80 °C for 24 h. The dried mixture was heated to 600 °C at the heating rate of 5 °C/min in horizontal furnace under nitrogen gas flow (80 ml/min) and held at this temperature for 2 h. Finally, the sample was washed with ethanol several times and then dried in a vacuum oven at 80 °C for 24 h. The schematic illustration of the preparation process can be seen in Fig. 1.

2.3. Characterization

The morphologies of all samples were characterized by field emission scanning electron microscopy (FESEM, JEOL 7500F, Japan) and transmission electron microscope (TEM, JEOL JEM-2100, Japan) with

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