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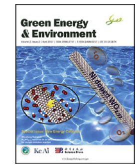

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Review article

Biomass derived porous nitrogen doped carbon for electrochemical devices

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Abstract

Biomass derived porous nanostructured nitrogen doped carbon (PNC) has been extensively investigated as the electrode material for electrochemical catalytic reactions and rechargeable batteries. Biomass with and without containing nitrogen could be designed and optimized to prepare PNC via hydrothermal carbonization, pyrolysis, and other methods. The presence of nitrogen in carbon can provide more active sites for ion absorption, improve the electronic conductivity, increase the bonding between carbon and sulfur, and enhance the electrochemical catalytic reaction. The synthetic methods of natural biomass derived PNC, heteroatomic co- or tri-doping into biomass derived carbon and the application of biomass derived PNC in rechargeable Li/Na batteries, high energy density Li–S batteries, supercapacitors, metal-air batteries and electrochemical catalytic reaction (oxygen reduction and evolution reactions, hydrogen evolution reaction) are summarized and discussed in this review. Biomass derived PNCs deliver high performance electrochemical storage properties for rechargeable batteries/supercapacitors and superior electrochemical catalytic performance toward hydrogen evolution, oxygen reduction and evolution, as promising electrodes for electrochemical devices including battery technologies, fuel cell and electrolyzer.

Keywords: Biomass; Nitrogen doped carbon; Batteries; Fuel cell; Electrolyzer

1. Introduction

Converting from biomass to energy usable materials has been extensively investigated because of the importance for academic research and industrial processes [1]. Biomass derived porous nanostructured carbon could be prepared by pyrolysis of various biomass and has been widely employed as the electrode materials for fuel cells and rechargeable batteries [2,3]. Commercialized rechargeable lithium-ion batteries (LIBs) with high energy density, long cycle life and good environmental compatibility, play the vital roles in our daily lives as the dominant power source for portable electronic devices and electric vehicles [4]. The aspiration of electrifying long-range vehicles is always driving us to explore novel electrode materials for high performance LIBs [5]. In the fuel cell technology, precious noble metal platinum (Pt) is considered as the most active material to overcome the sluggish oxygen reduction reaction (ORR) [6], even though considerable activation energy loss related can't be completely removed. The fuel cell technology has targeted tremendous efforts in inventing cost effective low-platinum or non-platinum group metal catalyst [7,8]. Porous nitrogen doped carbon (PNC) has been considered as a promising electrode for both rechargeable batteries and fuel cells [1,9]. As an example, the presence of nitrogen in carbon can increase the bonding between carbon and sulfur, which improves the capture capability of the product in the Lithium–Sulfur (Li–S) battery, resulting in a mitigation of the dissolved intermediate into the electrolyte [10]. The incorporation of nitrogen into carbon is also reported to increase the electronic conductivity to enhance the charge transfer, leading to a high charge–discharge rate and high durability of LIBs and

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supercapacitors (SCs) [9]. In addition, more active sites for ion absorption could be introduced during nitrogen doping process to obtain a high capacity or capacitance for LIBs or SCs [11]. Generally, four types of nitrogen-carbon groups including pyridinic, pyrrolic, graphitic (quaternary) were formed, accompanying the nitrogen doping. Pyridinic-N with lone electron pairs can weaken the O–O bond via side-on adsorption of oxygen molecules while the graphitic-N can enhance the electron transfer from the carbon electronic bonds to oxygen antibonding orbitals [12,13]. Both pyridinic-N and graphitic-N were believed to act as ORR sites and enhanced the ORR kinetics. Except for the carbon and water contents, various elements such as sulfur, nitrogen, iron, copper and cobalt in biomass can facilitate the formation of ORR active sites [7,14–17]. N- and C-containing biomass such as proteins, amino acids, peptides, and polysaccharides can be used as precursors for PNCs while pyrolysis and hydrothermal carbonization are two processes, which can covert biomass to PNCs [1].

In this review, the synthetic methods of natural biomass derived PNC materials for developing high performance electrochemical catalysts and energy storage devices will be summarized. Regarding the biomass derived PNC materials for rechargeable Li/Na batteries, we heavily discuss the synthesis of expanded carbon nanosheets from okara for Na-ion battery application. We then summarize the application of biomass derived PNC materials in high energy density Li–S batteries. We evaluate research efforts on supercapacitors and fuel cell (oxygen reduction and evolution reactions, hydrogen evolution reaction) using biomass derived PNC as the electrodes and heteroatomic co- or tri-doping into biomass derived carbon. We also provide the concluding remarks and prospects for the future development of using biomass derived PNC in developing high performance electrochemical catalysts and energy storage devices in the last section.

2. Synthesis methods and morphology of biomass derived PNC

2.1. Synthesis methods of PNC from biomass

The synthetic methods of converting biomass to porous nitrogen doped carbon have been reviewed by Antolini [1]. Biomass, an environmentally friendly and reproducible resource, has attracted much attention as the crude material to synthesize carbonaceous materials [18,19]. Hydrothermal carbonization (HTC) process is a unique thermochemical transformation process at specific conditions to convert biomass into carbonaceous materials, and has become one of the most widely used methods with demonstrated advantages [20,21]. HTC takes the advantages of simple, low cost, CO_2-netural process, and wet process (biomass could be used directly without expensive pre-drying process). However, HTC could process some wastes which require expensive disposal. Pyrolysis, a simple, low-cost technology capable of processing various biomass feedstocks, is another typical process to prepare PNC. However, a huge loss of N-containing precursors due to the emission of volatile gas will decrease the nitrogen contents in PNC [22]. Later a combination of HTC and pyrolysis was adopted. Basically, nitrogen elements were firstly stabilized in carbon via HTC at a lower temperature, then further pyrolyzed at a higher temperature. It is noted that the main drawback of PNC after the pyrolysis process lies on its low porosity and surface area. As a result, physical/chemical activation [23], templating [15] and sol–gel process [24] are proposed as effective countermeasures to increase the carbon porosity. Template synthesis of carbonaceous materials from biomass has been applied widespread and became a rapidly growing area. In the template synthesis, a nanoscale template with desired structures is filled with targeting material precursor, then subjected to the thermal treatment and the original template is finally removed. Combining physical/chemical activation and template routes, extra mesoporous could be achieved and the surface area would be significantly increased, leading to the enhanced charge and ion transfer [18]. Fig. 1 illustrated a representative example to synthesize highly ordered PNC. SBA-15 template with ordered pore structure was filled with precursor. After carbonization and etching process, a hierarchical PNC was obtained. The sulfur doped PNC was achieved by activating PNC with KOH activation and fused with sulfur. The sulfur-PNC composite was demonstrated as a promising electrode for lithium sulfur batteries.

Chitosan derived PNC could be obtained by combining HTC and pyrolysis method with SiO_2 as template [25]. Gelatin derived PNC takes the advantages of various methods to optimize electrochemical performance and porous structure [26]. Ionic liquids have also emerged as an energy saving and environmental benign method to prepare PNC. The ionic liquids interact with solutes to form hydrogen bond as a result of the miscibility of polar solutes with –NH groups. Besides, ionic liquids containing nitrogen group are also used as nitrogen source during the PNC synthesis [27,28].

2.2. Biomass sources and morphology of PNCs

Except for nitrogen containing precursor (e.g. bacteria cellulose) [29], another main sustainable biomass without nitrogen source such as lignin should be introduced nitrogen containing functional group or under the ammonia gas during pyrolysis process so as to prepare nitrogen doped carbon [30]. Lignin is the one of the most abundant organic aromatic polymer on earth and can constitutes up to 35 wt% of the dry mass of wood. However, the preparation of nitrogen doped carbon (NDC) is not straightforward from lignin and can only be achieved by the reaction with a second nitrogen-containing precursor since lignin naturally lacks nitrogen functionalities [31]. However, unexpected poor homogeneity of the final materials is one of the drawbacks associated with the approach due to the absence of molecular mixing. It was reported that cheap and sustainable lignin-based NDCs could be prepared by the covalent functionalization of lignin with nitrogen containing groups [30]. The isolation of lignin from beech wood chips will further be achieved via alkaline hydrothermal treatment, whereafter treated by a straightforward aromatic