



Direct carbonization of rice husk to prepare porous carbon for supercapacitor applications



Wenli Zhang^{a, b}, Nan Lin^{c, **}, Debo Liu^a, Jinhui Xu^a, Jinxin Sha^a, Jian Yin^a, Xiaobo Tan^d, Huiping Yang^d, Haiyan Lu^a, Haibo Lin^{a, b, *}

^a College of Chemistry, Jilin University, No.2699 Qianjin Street, Changchun 130012, China

^b Jilin Kaiyu Electrochemical Energy Storage Technologies Development Co., Ltd., No.5188 Guigu Street, Changchun 130012, China

^c Institute of Energy and Process Systems Engineering, Technische Universität Braunschweig, Franz-Liszt-Str. 35, Braunschweig, Germany

^d Zhejiang Meineng Electric Co., Ltd., Tianzihu Industrial Park, Anji 313309, China

ARTICLE INFO

Article history:

Received 24 July 2016

Received in revised form

15 March 2017

Accepted 12 April 2017

Available online 18 April 2017

Keywords:

Rice husk

Porous carbon

Supercapacitor

Self-activation

Energy storage

ABSTRACT

Searching low-cost porous carbon is crucial for the future development of supercapacitors in a wide application range. In this paper, rice husk derived carbon (RHC) was prepared through direct carbonization of rice husk in a tube furnace without inlet of N₂. RHC possesses relatively high pore volume, specific surface area and specific capacitance. The high specific surface area of RHC is attributed to the self-activation of rice husk by H₂O, CO₂ produced in the carbonization process. RHC was further treated by alkali etching to prepare a porous carbon (referred as RHPC). Owing to the removing of SiO₂ in RHC, RHPC exhibits higher specific surface area and specific capacitance than RHC.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

For the past decades, the research of supercapacitors has achieved much attention in the realms of mechanisms and materials. However, supercapacitors still face to two dilemmas: (1) relatively low energy density compared with rechargeable batteries; (2) high cost of electrode materials and electrolytes. As a result, supercapacitors only occupy a niche market of energy storage devices [1]. From the point of view of cost, the cost of every round-trip energy storage process per unit energy (Watt-hour) should be lowered to its farthest. The energy storage cost per unit Watt-hour for every energy storage process is defined as follows:

$$Es = \frac{\text{Cost}}{\text{Energy} \times \text{Cycle}} \quad (1)$$

In order to lower the energy storage cost of supercapacitors, the

research and development trends of supercapacitor have been focused on the following issues: (1) enhancing energy density; (2) prolonging cycle life; (3) lowering the cost of electrode materials, electrolytes and other modules of supercapacitors. In order to enhance the energy density of supercapacitor, materials with high specific capacitance [2] and organic electrolytes which enable supercapacitor with high operating voltage are applied [3]. A very important strategy to improve the energy density of supercapacitor is choosing asymmetric design [4]. For unstable electrode materials, the improvement of electrode stability is very necessary [5,6], since, the enhancement of cycling stability could lower the energy storage cost of supercapacitors. The above strategies could enhance the denominator of Eq. (1), thus, could lower the energy storage cost. Another important strategy is to lower the cost of electrode materials so as to endow supercapacitor low energy storage cost. From this point of view, new preparation methods should be developed to produce low-cost materials. These methods should use less energy and chemicals.

Porous carbon is a commercial electrode material for supercapacitor. Porous carbon, mainly refers to activated carbon, is generally prepared via carbonization-activation method [7–9]. Carbonization process is simple and of low-cost owing to the low

* Corresponding author. College of Chemistry, Jilin University, No.2699 Qianjin Street, Changchun 130012, China.

** Corresponding author. Institute of Energy and Process Systems Engineering, Technische Universität Braunschweig, Franz-Liszt-Str. 35, Braunschweig, Germany.

E-mail addresses: n.lin@tu-braunschweig.de (N. Lin), lhb910@jlu.edu.cn (H. Lin).

heat-treatment temperature (usually, from *ca.* 500 °C to *ca.* 1000 °C). However, activation process is expensive due to the use of a large amount of activation agents (Scheme 1), such as NaOH, KOH, ZnCl₂ and H₃PO₄. Although, by activation process, activated carbon can obtain a high surface area as large as 1000–3000 m² g⁻¹ [7–9], the application of activation agent would result in the high cost of activated carbon. It is estimated that the activation agent occupies most of the cost of porous carbon. Besides, the emission of large amount of alkali effluent would do harm to the environment. Hence, an ideal preparation method of activated carbon should not include activation process. Direct carbonization is preferable for the preparation of activated carbon (Scheme 1) due to the simplified route and the decreased chemicals.

Various researchers choose direct carbonization method to prepare porous carbons [10–14]. This approach has been applied to certain organics and biomasses, such as, potassium biphthalate [10], condiment [11], potassium citrate [12], metal-organic frameworks [13], seaweeds [14], and etc. Unfortunately, due to the shrinkage effect during carbonization process, the carbonization of most abundant biomasses can only obtain carbons with low surface area [7]. The application of lignin, cellulose and other useless biomasses (such as rice husk and straw) in the preparation of porous carbon is of significance for the concerns of environmental protection and sustainable development. Direct carbonization of cellulose and lignin to prepare porous carbon has been approved to be an effective, general way to prepare porous carbon used in supercapacitors [15,16]. The highly porous structure of carbon originates from the “self-activation” process of lignin and cellulose. Namely, the decomposition products of H₂O and CO₂ from cellulose and lignin act as activation agent in the heat-treatment process. In literature [16], this process is called self-activation.

Rice husk is an abundant biomass, and is almost useless when it is peeled off from rice grain. Rice husk is of low combustion value when it is used as fuel. The burn of rice husk in the field also causes damage to the environment. So, the sustainable and comprehensive utilization of rice husk is the research hotspot [17–21]. Rice husk is composed of lignin, cellulose, hemicellulose and a unique component SiO₂ with a weight percentage of *ca.*15–20 wt% [22]. These SiO₂ in rice husk exists in micro- and nano-scale. Hence, rice husk is a kind of natural organic-inorganic composite. Various researchers have

used rice husk as precursor to prepare porous carbon by carbonization-activation method [23–28]. Carbonization-activation method is expensive and not environmentally friendly for the preparation of porous carbon. Although, the involvement of comprehensive utilization strategy could reduce the use of activation agent and the emission of high alkali effluent, these processes are complicated [20,21].

In this paper, a direct carbonization method was applied in the preparation of rice husk derived carbon (denoted as RHC). RHC was further treated by alkali etching to prepare a porous carbon (denoted as RHPC). These two kind of porous carbons exhibit relatively high porosity, high specific surface area and high specific capacitance. Meanwhile, the preparation of RHC and RHPC is of low-cost, and has further potential to be developed and used in supercapacitors.

2. Experimental

2.1. Preparation of RHC and RHPC

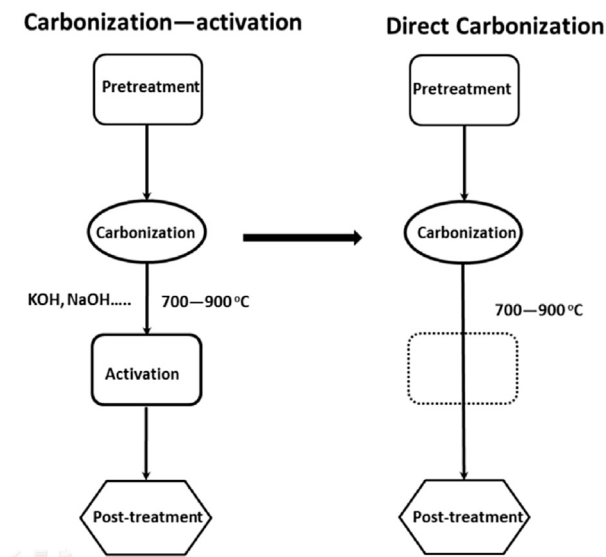
Rice husk was collected from a factory in Changchun city (Jilin Kaiyu Biomass Development Co., Ltd.). Other chemicals were analytical grade reagents. Before heat treatment, rice husks were washed with deionized water and dried in a drying oven at temperature of 100 °C for 10 h. Rice husks without grinding were filled in a porcelain boat (width: 20 mm, length: 45 mm and height: 15 mm) and put into a tube furnace (inner diameter of 55 mm). N₂ flow was used to exclude the air in the tube for half an hour. During and after heat treatment, N₂ was no longer injected into the tube. Thermogravimetric curve was conducted to study the pyrolysis process of rice husk, the pyrolysis temperature was set at 800 °C (See Supporting Information, Fig. S1). Rice husks were heat-treated at 800 °C for 2 h and the heating rate is set as 10 °C min⁻¹. The obtained carbon materials were denoted as RHC. RHC was ground to micrometer-sized particles and was further treated by alkali etching in 10 wt% NaOH solution (liquid to solid mass ratio of 10:1) at 100 °C for 2 h to eliminate most of the residual SiO₂ in RHC. After drying, the rice husk derived porous carbon (denoted as RHPC) was obtained.

2.2. Physical characterization

The morphology of RHC and RHPC was observed with a field emission scan electron microscope (SEM) (SU8020, Hitachi, Japan). X-ray energy dispersive spectra (EDS) was obtained via Quantax EDS spectroscopy (Bruker, Germany) coupled with SEM. The pore size distribution and specific surface area of RHC and RHPC were tested via N₂ adsorption desorption machine (JW-BK132F, Beijing JWGB Sci. & Tech. Co., Ltd, China). Specific surface area was calculated via Brunauer-Emmett-Teller (BET) model, the microporous parameters were calculated via Horvaih-Kawazoe (HK) method and mesoporous parameters were calculated via Barrett-Joyner-Halenda (BJH) method.

2.3. Electrochemical characterization

First, the as-prepared carbon material was mixed with conductive agent (acetylene black) and binder (PTFE) with a mass ratio of 85:10:5 in ethanol. Ethanol was then evaporated while stirring, finally a dry mixture was obtained. The mixture was then rolled into a sheet with the help of ethanol soaking. The sheet was dried at 90 °C overnight, and then cut into small sheets with geometric area of 1 × 1 cm². The small carbon sheets were pressed on nickel foams with a pressure of 15 MPa. The mass loading of carbon sheet was *ca.* 5 mg cm⁻². Symmetric supercapacitors were



Scheme 1. Flow chart of carbonization-activation method and direct carbonization method for the preparation of porous carbon.

Download English Version:

<https://daneshyari.com/en/article/5476056>

Download Persian Version:

<https://daneshyari.com/article/5476056>

[Daneshyari.com](https://daneshyari.com)