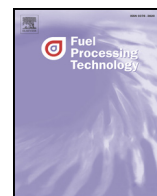




Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Lignite-derived high surface area mesoporous activated carbons for electrochemical capacitors

Bao-Lin Xing^{a,c}, Hui Guo^a, Lun-Jian Chen^a, Zheng-Fei Chen^b, Chuan-Xiang Zhang^{a,*}, Guang-Xu Huang^a, Wei Xie^c, Jiang-Long Yu^{c,*}^a School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454003, Henan, China^b Newcastle Institute for Energy and Resources, The University of Newcastle, Callaghan, NSW 2308, Australia^c Chemical Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia

ARTICLE INFO

Article history:

Received 24 April 2015

Received in revised form 9 July 2015

Accepted 13 July 2015

Available online xxx

Keywords:

Lignite

Mesoporous activated carbon

Electrochemical capacitors

Electrochemical performance

ABSTRACT

Mesoporous activated carbons (ACs) were successfully prepared from lignite using KOH as activation agent at the temperature above 700 °C. The pore structure and surface chemistry of the as-prepared ACs were characterized by means of nitrogen adsorption–desorption, X-ray diffraction, scanning electron microscope, transmission electron microscope and X-ray photoelectron spectroscopy. The results show that such prepared mesoporous ACs have a high specific surface area ($\sim 3036 \text{ m}^2 \cdot \text{g}^{-1}$) with a hierarchical macro–meso–micro-pore structure and oxygen-enriched surface. The electrochemical performances of the ACs as electrode materials for electrochemical capacitors (ECs) were assessed by galvanostatic charge–discharge, cyclic voltammetry and cycling durability tests. It was demonstrated that the mesoporous ACs produced in this study possessed a maximum specific capacitance of $355 \text{ F} \cdot \text{g}^{-1}$ and $196 \text{ F} \cdot \text{g}^{-1}$ in 3 M KOH aqueous and 1 M $(\text{C}_2\text{H}_5)_4\text{NBF}_4/\text{PC}$ organic electrolytes, respectively, at a current density of $50 \text{ mA} \cdot \text{g}^{-1}$, and exhibited a desirable energy and power density with a superior cycling performance. The excellent capacitive behavior of the prepared mesoporous ACs in aqueous system is attributed to their unique macro–meso–micro-hierarchical pore structure with high surface area and oxygen-containing surface. Their superb electrochemical performance in the organic electrolyte is attributed to their well-developed mesoporous structure.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The excessive use of fossil fuels has increased the risks of global energy crisis and environmental pollution and has led to an urgent need for sustainable energy sources and new technologies for energy conversion and storage. Electrochemical capacitors (ECs), also called supercapacitors or ultracapacitors, have drawn much attention as alternative energy storage devices due to their high power density, desirable coulombic efficiency, excellent cycling life and environmental friendliness [1–3]. ECs have widespread applications in the hybrid electric vehicles, portable electronics, high power electronic devices and uninterruptable power supplies [4]. The performance of ECs is greatly affected by the structure and property of their electrode materials, such as activated carbons (ACs), carbon nanotubes, carbon aerogels, graphene, transition metal oxides and conducting polymers [5–11]. Among these materials, ACs derived from various carbonaceous precursors are preferred due to their high surface area, superior chemical stability, excellent conductivity as well as relatively low cost and good accessibility [12,13]. However, the

lower energy density of ECs using ACs electrode materials compared to that of rechargeable lithium batteries has limited their use in large-scale applications [14,15]. Therefore, it is crucial to develop high performance ACs with high energy density to improve the performance of such ECs.

The energy storage of ECs using ACs as electrode materials can be achieved by accumulating electrostatic charge in the electric double layers at the electrolyte/electrode interface [16]. ACs with high specific surface area would lead to high specific capacitance for ECs. However, some micropores (less than 2 nm) in ACs may not be accessible for the electrolyte ions due to the narrow pore ‘gate’ effects at the pore entrance [15,17], especially in high surface area ACs, leading to lower capacitance. Therefore, the pore structure of ACs is a critical factor which determines the electrochemical performance of ECs [15,18]. The micropores in ACs electrode materials, usually accounting for a high specific surface area, play an essential role in the adsorption of electrolyte ions to achieve high capacitance; whereas the mesopores (2–50 nm) are necessary for the diffusion of the electrolyte ions into the bulk materials, which will in turn improve the accessibility of the micropores [19–21]. Furthermore, the mesopores also serve as the channel for ion diffusion and facilitate fast electrolyte ions transport, thereby achieving the electrochemical performance of ECs at a high rate [22]. Consequently, high

* Corresponding authors.

E-mail addresses: zcx223@hpu.edu.cn (C.-X. Zhang), jianglong.yu@newcastle.edu.au (J.-L. Yu).

surface area ACs enriched in mesopores are desirable for high performance ECs.

Mesoporous ACs with various pore structures as ECs electrode materials exhibiting outstanding capacitive performance and superior rate capability have been recently reported [23–28]. These mesoporous ACs are generally prepared by hard or soft template methods. The hard template method for preparing the mesoporous carbons involves the infiltration of carbon sources into silica or zeolite followed by carbonization and template removal. By comparison, the mesopores in carbons from the soft template method are produced via self-assembly of surfactant prior to template removal by heat treatment [29,30]. However, it is difficult for large-scale production and industrial applications of these types of mesoporous ACs due to the complicated synthesis route and high cost of templates [4], despite that these mesoporous ACs have highly uniform pore size distribution. It therefore becomes necessary to produce mesoporous ACs using a cost-effective process without using templates.

Coal is the most popular precursor for producing ACs owing to its abundance, low cost and high carbon content. Generally, there are two processes for the preparation of ACs from coal: physical activation and chemical activation. The former involves carbonization of coal under an inert atmosphere followed by activation of the resulting char at a high temperature about 800–1000 °C in the presence of activating agents such as steam, carbon dioxide, air or their mixtures [31,32]. The latter generally produces ACs through impregnating coal with dehydrating reagents such as KOH, ZnCl₂ and H₃PO₄ and carbonized at desired conditions in an inert atmosphere [33]. Compared to the physical activation, the chemical activation has several advantages including single step activation process, low activation temperature, short activation time, high yield and easy to obtain well-developed porosity [34]. Among various activation reagents, KOH is recognized as an effective activating agent for producing coal-based ACs with extremely high surface area, but these ACs often have microporous structures [35].

It is well known that the pore structure of ACs is not only dependent on the preparation process but also on the carbonaceous precursors. As an inexpensive carbonaceous material, lignite is abundant and has low calorific value, high water content and volatile matter content, loose sponge texture and high chemical reactivity [36,37]. It could be a promising precursor for the production of mesoporous ACs. However, there has been little information available in the open literature regarding the preparation of mesoporous ACs from lignite.

This paper reports the successful production of mesoporous ACs with high surface area from lignite by KOH activation. The pore structure, microstructure and surface chemistry of the mesoporous ACs were investigated in detail. The electrochemical performances of the ECs assembled from these AC electrode materials were also evaluated in both a 3 M KOH aqueous electrolyte and 1 M (C₂H₅)₄NBF₄/PC organic electrolyte in terms of galvanostatic charge–discharge, cyclic voltammetry and cycling durability.

2. Experimental

2.1. Materials

A lignite coal from Indonesia was used as the precursor without further purification. The results of proximate and ultimate analyses are given in Table 1. Thermogravimetric (TG) analysis of lignite was

Table 1
Proximate and ultimate analyses of lignite.

Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
M _{ad}	A _d	VM _{daf}	C	H	O ^a	N	S
14.91	4.35	48.42	67.76	4.57	22.82	1.29	3.56

ad, air dry basis; d, dry basis; daf, dry and ash-free basis.

^a By difference.

conducted by using a Netzsch STA409 PC thermogravimetric analyzer at a flow rate of 50 ml·min⁻¹ from room temperature to 800 °C under nitrogen, and the results are shown in Fig. S1. The residual carbon yield was 58.3 wt.%, indicating that the lignite is a suitable precursor for the preparation of ACs. Commercially available KOH (analytical grade) was supplied by Tianjin Kemiou Chemical Reagent Co., Ltd., China. High purity nitrogen (99.999%) and deionized water were used throughout the experiments. For the purpose of comparison, a commercial microporous AC (Maxsorb; Kansai, Japan) was selected as a reference.

2.2. Preparation and characterization of ACs

The lignite was crushed and sieved into a particle size range of 100–180 μm, and then was impregnated with a KOH aqueous solution to obtain a mixture with a 4:1 mass ratio of KOH to lignite. The mixture was placed in a nickel reactor and heated at 200 °C for 1 h to dehydrate, followed by further heating to 600 °C, 700 °C or 800 °C at a heating rate of 5 °C·min⁻¹ in a high purity nitrogen flow and held for 1 h. The sample was then cooled to room temperature, and was subsequently washed with 5 M HCl solution and deionized water until the pH of the solution was neutral. The sample was then dried in vacuum at 200 °C for 4 h. Such prepared AC samples were denoted as AC_x, where X represents the activation temperature. The schematic diagram of experimental apparatus for preparing ACs is shown in Fig. 1.

The Brunauer–Emmett–Teller (BET) specific surface area and total pore volume of the ACs were measured from nitrogen adsorption isotherms at -196 °C on a Micromeritics ASAP 2020 automatic adsorption instrument. Micropore surface area and volume were obtained by *t*-plot method, and the pore size distribution was evaluated by the density functional theory (DFT) from the adsorption branch. All samples were degassed in vacuum at 200 °C for 10 h prior to the nitrogen adsorption analysis. A JSM-6390LV scanning electron microscope (SEM) and a JEM-2100 transmission electron microscope (TEM) were employed to examine the morphology of ACs. X-ray diffraction (XRD) analysis of raw coal and AC samples was carried out using a Bruker D8 Advance diffractometer with a Cu Kα X-ray radiation source, operated at 40 kV and 40 mA. The elemental compositions and surface chemistry of AC samples were analyzed by an elemental analyzer (Vario Macro Cube, Germany) and a Perkin Elmer X-ray photoelectron spectroscopy (XPS) with Al Kα X-ray radiation.

2.3. Electrochemical characterization

The electrochemical performances of the AC samples including Maxsorb were investigated using two-electrode Swagelok-type cells

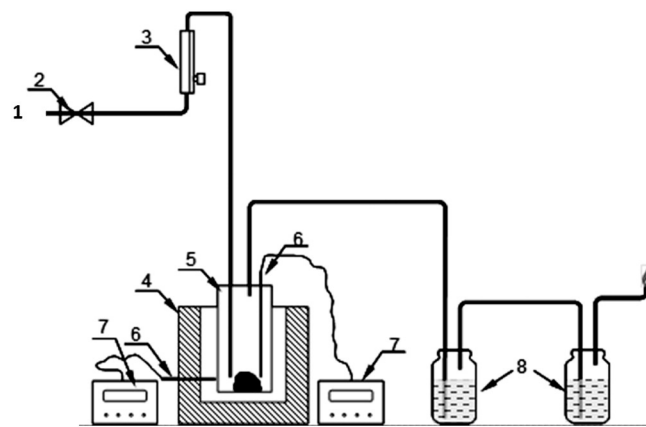


Fig. 1. Schematic diagram of the experimental apparatus for preparing ACs: (1) Nitrogen gas; (2) Regulator; (3) Gas flowmeter; (4) Electric furnace; (5) Nickel reactor; (6) Thermocouple; (7) Temperature controller; (8) Gas scrubber.

Download English Version:

<https://daneshyari.com/en/article/6656967>

Download Persian Version:

<https://daneshyari.com/article/6656967>

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