A novel melt infiltration method promoting porosity development of low-rank coal derived activated carbon as supercapacitor electrode materials

Lijie Wang, Fei Sun*, Jihui Gao*, Xinxin Pi, Tong Pei, Zhipeng Qie, Guangbo Zhao, Yukun Qin

School of Energy Science and Engineering, Harbin Institute of Technology, Harbin 150001, Heilongjiang, China

A B S T R A C T

Focusing on the bottlenecks of traditional physical or chemical activation methods for the preparation of activated carbons, we report a simple and scalable melt infiltration strategy assisted with CO_2 activation for the preparation of activated carbons from Chinese large-scale reserve Zhundong coal. The preparation is achieved by the melt infiltration of a small amount of anhydrous $FeCl_3$ (10–20 wt%) into the coal framework and subsequent CO_2-assisted physical activation during which the encapsulated iron species play the dual role of pore-forming templates and activating catalysts. The as-obtained MI-AC-2 possesses a partially hierarchical pore structure with a high specific surface area of 1872 m^2 g^{-1}, five times more than the activated carbon prepared by solely physical activation, which endows the constructed MI-AC-2 electrode with good supercapacitive performances. Relative to the large consumption of activation agents used in a traditional chemical activation process, such a new method with low-cost resource materials and the low-dose $FeCl_3$ additive paves a scalable way to loading metal precursor into coal/biomass for the preparation of high-porosity activated carbons. This work also provides a simple and efficient strategy to encapsulate active materials into external matrix or substrate.

© 2018 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Carbonaceous materials, due to their high physicochemical compatibility, easily-tunable porosity and framework and environmentally benign nature, have been extensively explored and applied in the fields of gas adsorption [1–4], electrochemical energy storage [5–8] and catalysis [9–11]. To date, various types of carbonaceous materials such as graphite [12], activated carbons [2–5,9], ordered mesoporous carbons [13,14], carbon fibers [15], fullerene [16] and graphene [17,18] have shown progress in carbon materials science and engineering. Among them, activated carbons derived from various types of biomass/coals have the advantages of low-cost and facile production, thus inducing people to extend their applications from ancient times to the present [4,19].

Take supercapacitor as an example, it stores charges by the electrostatic adsorption or accumulation of electrolyte ions onto the surface of activated carbon electrodes [7]. According to the capacitance calculation equation ($C = \varepsilon S/d$), high porosity and large specific surface area (SSA) can promote the value of capacitance [20,21]. Hence, some high surface area activated carbons [22] or

heteroatom-doped activated carbons [19] were successfully synthesized based on controllable physical or chemical activation methods. These activated carbons show improvements in boosting the capacitance of constructed electrodes. However, the current physical or chemical activation methods for preparing activated carbons have two main bottlenecks. Firstly, traditional physical activation methods employing H_2O, CO_2, flue gas or their mixtures as activation agents often leads to the resulting activated carbons having low porosity and a specific surface area less than 1000 m^2 g^{-1} [2]. Secondly, frequently-used chemical activation process, producing high surface area activated carbon via adding a large amount of chemical activation agents (such as KOH [22,23], K_2CO_3 [24,25], $ZnCl_2$ [26] and H_3PO_4 [27]), it subsequently needs much water/acid consumption to remove the residual activation agents, which increases the difficulties of industrial-level production and environmental governance. Thus, it is desirable to develop new strategies for preparing high porosity/surface area activated carbons to overcome the weakness of traditional physical or chemical activation crafts.

Low-grade coals, featuring high reserve, medium calorific value, higher volatile matter and high reactivity, are superior precursor candidates for preparing activated carbons. For example, Zhundong coal in Chinese Xinjiang District has an exploitable reserve of 164 Gt and an unripe, easily-tunable coal framework [28]. In

* Corresponding authors.
  E-mail addresses: sunf@hit.edu.cn (F. Sun), gaojh@hit.edu.cn (J. Gao).

our previous study, a one-step ammonia activation method was utilized to prepare Zhundong coal-derived N-doped microporous carbons which show excellent performances as gas adsorbents and electrochemical energy storage materials [1]. In this study, we demonstrated a novel melt infiltration method to promote the porosity development of Zhundong coal-based activated carbons. The preparation process involves the melt infiltration of anhydrous $FeCl_3$ into the coal framework and subsequent CO_2-assisted physical activation, during which the embedded iron species play the dual role of pore-forming templates and activating catalysts. Such a melt infiltration strategy endowed the resulting activated carbon (denoted as MI-AC-2) with a greatly increased specific surface area, five times more than that of the activated carbon (denoted as AC) produced by solely physical activation. Particularly noteworthy is that the mass fraction of $FeCl_3$ additive is only 10–20% of the coal precursor, much lower than the dose of activation agents used in the traditional chemical activation process. Evaluated as supercapacitor electrode materials, the as-obtained MI-AC-2 shows high capacitances, good rate capability and excellent cycling stability.

2. Experimental section

2.1. Synthesis of MI-ACs, AC and LI-AC

Zhundong coal, a kind of low-rank coal, is rich in humic acid structures that contain numerous side chains or functional groups linked to benzene rings. The proximate and ultimate analysis results for raw Zhundong coal are given in Table S1, indicating relatively high volatile component. The ash compositions for raw Zhundong coal are given in Table S2. For the synthesis of Zhundong coal based activated carbons, the raw coal with particle size less than 1 mm first underwent a hydrochloric acid (5 M) and hydrofluoric acid (20 wt%) treatment procedure with stirring at 50 °C for 12 h to remove the minerals [29]. As can be seen from Fig. S1, some less apparent peaks appeared in the XRD pattern of ZD coal, while the XRD pattern of ZD-HCF was relatively smooth without obvious peaks, which indicated that minerals in raw coal sample have been removed. For the synthesis of MI-ACs, a melt infiltration method was employed. In a typical procedure, anhydrous $FeCl_3$ (Aladdin) and coal powders with a certain mass ratio were mixed and grinded to get a homogeneous mixture, which was then transferred to a glass vial and vacuumized for 1 h. Subsequently, the vial was then sealed under vacuum and heat-treated at 350 °C for 1 h (Fig. S1). Because the molten and boiling point of anhydrous $FeCl_3$ is relatively low, which is 305 °C and 312 °C, molten or gasified anhydrous $FeCl_3$ could penetrate into the framework of coal sample by capillary force under high-temperature vacuum condition. After cooling down, the sample in the vial was transferred into a crucible in a horizontal furnace, which was then activated at 900 °C for 1 h under a mixture of CO_2 and N_2 atmosphere (including 120 mL min^{-1} N_2 and 80 mL min^{-1} CO_2) with a heating rate of 10 °C min^{-1}. During the CO_2-assisted activation, the entrapped and dispersible iron species could catalyze the reaction between coal skeleton and CO_2 and promote the pore formation. Then the activated samples underwent a washing (2 M HCl and de-ionized water) and drying procedure to yield the MI-ACs (Fig. S2). Some new pores were released during the removal of iron-based components in the process of washing. Compare with the traditional liquid impregnation, this method could ensure the formation of small Fe-containing crystals uniformly dispersed and confined in the coal inner structure, thus leading to the resulting activated carbon with high porosity. By changing the $FeCl_3$-to-coal mass ratio from 1:10, 2:10 to 3:10, in the melt infiltration process, MI-AC-1, MI-AC-2 and MI-AC-3 were prepared, respectively.

Control samples (AC and LI-AC) to demonstrate the melt infiltration effect on the porosity development of MI-ACs, a solely physical activation procedure (similar to the above process but without the melt infiltration steps) was used to obtain the activated carbon (denoted as AC) for comparison. Moreover, a liquid impregnation method was used to prepare the activated carbon (denoted as LI-AC). To be specific, a pre-weighed amount of mineral-free coal was added into the solution of $FeCl_3$ to make a coal-water slurry ($FeCl_3$-to-coal mass ratio of 1:5) during magnetic stirring. Then the coal-water slurry was dried at 80 °C with magnetic stirring of 300 r min^{-1} until the water completely evaporated. The obtained $FeCl_3$-coal mixture then underwent the same CO_2-assisted physical activation process as MI-ACs. A comparing schematic for illustrating the preparation process of $FeCl_3$-coal mixture between melt infiltration and liquid impregnation can be seen in Fig. S1.

2.2. Characterizations

Scanning electron microscopy (SEM, Helios Nanolab600i) with energy dispersive X-ray apparatus and transmission electron microscopy (TEM, JEM-2100) were adopted to record the morphology and inherent mineral distribution of the samples. N_2 adsorption/desorption isotherms of the resulting samples were measured at −196 °C using ASAP 2420 (V2.05) apparatus. The BET surface area was calculated from the isotherm according to the Brunauer–Emmett–Teller equation [22]. The micropore volume (V_{mic}) was estimated by the Horvath–Kawazoe (HK) method. The total pore volume (V_{total}) was calculated from the N_2 amount adsorbed at relative pressure of 0.975. Pore size distribution was calculated based on Density Functional Theory (DFT) [30]. X-ray diffraction (XRD) patterns were measured on a Rigaku D/Max 2400 diffractometer using CuKa radiation (40 kV, 40 mA, λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5700 ESCA System with Al Ka X-ray at 14 kV and 6 mA.

Thermogravimetric analysis (TGA) was conducted to record the weight loss of coal or coal-iron mixture by simulating CO_2-assisted physical activation process mentioned above. Typically, 10 mg of coal or coal-iron mixture was heated at a heating rate of 10 °C min^{-1} until 900 °C holding 1 h with a gas mixture of 40 mL min^{-1} CO_2 and 60 mL min^{-1} N_2 flowing through. Carbon conversion was calculated by the following equation [31]:

$$X_t = \frac{W_0 - W_t}{W_0 - W_{resi}} \tag{1}$$

Where X is carbon conversion, W_0 is the initial sample mass, W_t is the sample mass at the time of t, and W_{resi} is the mass of residual after activation process. Reactivity of coal was evaluated by the normalized reaction rate [32] as the following equation:

$$K_t = \frac{dX_t/dt}{1 - X_t} \tag{2}$$

Where K_t is the normalized reaction rate (min^{-1}), dX_t/dt is the reaction rate, and X_t is the carbon conversion at time t.

2.3. Fabrication of electrodes and electrochemical measurement

The electrochemical performances of the obtained activated carbons were determined in a three-electrode system with a basic aqueous solution (6 M KOH). For the fabrication of electrodes, the active material (80 wt%), carbon black (10 wt%), and polytetrafluoroethylene (PTFE) (10 wt%) were homogeneously mixed and rolled into a thin film. The above thin film was dried at 100 °C for 12 h and then pressed onto a nickel foam with a mass loading of 3 mg cm^{-2} as the working electrode. Pt foil and a saturated calomel electrode (SCE) electrode were used as the counter electrode and reference electrode, respectively [21]. All the electrochemical tests were conducted at room temperature. Galvanostatic charge/discharge (GC), cyclic voltammetry (CV), and electrical impedance spectroscopy (EIS) studies were all performed using