



The key pre-pyrolysis in lignin-based activated carbon preparation for high performance supercapacitors



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HIGHLIGHTS

- Lignin-based activated carbon was prepared with pre-pyrolysis for supercapacitor.
- Pre-pyrolysis improved both $V_{\text{micro}}/V_{\text{total}}$ and graphitization degree of LAC-P.
- LAC-P exhibited a high gravimetric capacity of 312 F g^{-1} .
- The capacity of LAC-P maintained 233 F g^{-1} even at 100 A g^{-1} .
- An outstanding stability was obtained with 95% retention ratio after 10,000 cycles.

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ABSTRACT

Lignin as second most abundant natural polymer after cellulose is the main by-product of conventional pulp and paper industry and mostly consumed as a low-grade fuel in industrial burner or boiler. It is necessary to explore the possibility for high value-added application of lignin. Lignin-based activated carbon (LAC) is prepared through a two-step pre-pyrolysis and activation or directly activation method for high-performance supercapacitors (SCs). This paper is devoted to examining the role of pre-pyrolysis treatment in the preparation of LAC. Pre-pyrolysis treatment is expected to alter the pore size distribution, maintain the morphology and improve the graphitization degree of lignin. Multiple characterization methods are used to measure the pore structure, morphology and graphitization degree of LAC. Consequently, LAC with pre-pyrolysis exhibits high $V_{\text{micro}}/V_{\text{total}}$ ratio, uniform morphology and relatively high graphitization degree in comparison with directly-activated LAC. In detail, The $V_{\text{micro}}/V_{\text{total}}$ ratio of LAC with pre-pyrolysis at $600 \text{ }^\circ\text{C}$ has increased from 22% to 66%. What's more, the gravimetric capacitance reaches to as high as 312 F g^{-1} by improving 100 F g^{-1} , the specific capacitance is $14.0 \mu\text{F cm}^{-2}$, and even after 10,000 cycles at 1 A g^{-1} a specific capacity of 261 F g^{-1} (about 95% retention ratio) remains while directly-activated LAC is only 218 F g^{-1} . Hence, LAC with pre-pyrolysis is a promising material for high performance SCs.

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1. Introduction

SCs, based on electrostatic adsorption of the electrolyte ions at the electrode interface, are indispensable components for electrical equipment and hybrid vehicles due to high power capability, fast charge/discharge rate and long cycle life. The excellent

performances of SCs mainly depend on high specific surface area (SSA), reasonable pore size distribution and high conductivity of active materials. Porous carbon is one of the most potential electrodes due to the abundant low-cost carbon precursors, stable surficial physicochemical properties and good conductivity.

Lignin as second most abundant natural polymer after cellulose is the main by-product of conventional pulp and paper industry and mostly consumed as a low-grade fuel in industrial burner or boiler. It comprises of a three-dimensional cross-linked structure through ether bonds or C–C linkages between phenyl propane monomers, i.e. guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl (H) unit [1,2].

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Both physical and chemical activation have been used to obtain high-SSA LAC [3,4]. KOH activation is especially known as a convenient and efficient way to obtain high-SSA together with high density activated carbon (AC). LAC electrode has been reported in some literature, such as Pluronic F127 template method [5] and the electrospinning method of alkaline lignin [6]. The obtained porous carbon may stand out in porosity distribution or energy density. However, the complicated procedures enlarge the cost to a great extent and make the high yields formidable, which is adverse to the intention of green energy strategies. An interesting phenomenon is found by the authors that AC with pre-pyrolysis treatment can obtain a rather high gravimetric capacity (C_g) above 300 F g^{-1} at low current density [7–9]. But the result is neglected and the mechanism of pre-pyrolysis is not investigated further due to the relatively weak performance at high current density. Besides, LAC for hydrogen electrosorption from lignin was also produced by standard carbonization and KOH activation by K. Babeř [10]. However, the influence of standard carbonization on the structure of LAC did not explain clearly.

Herein, we prepare LAC through two-step pre-pyrolysis and activation process in this work. Pre-pyrolysis treatment is expected to alter the pore size distribution and improve the graphitization degree of LAC [11,12]. And the influence of pre-pyrolysis treatment is characterized by multiple characterization methods such as Brunauer–Emmett–Teller (BET), Field emission scanning electron microscope (FESEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy etc. Cyclic voltammetry (CV), galvanostatic charge/discharge, cycle performance and electrochemical impedance spectroscopy (EIS) are also tested to evaluate the electrochemical performances of LAC. Thereafter, it is concluded that the pre-pyrolysis is a meaningful process to prepare samples with both excellent pore structure and electrochemical performance, which shows a great potential for application in SCs.

2. Materials and methods

2.1. Raw materials

Lignin precursor was provided by a chemical plant in Shandong province, China. Table 1 contains the main properties of the lignin precursor. The elemental analysis of the lignin precursor indicates it was composed mainly of carbon and an amount of hydrogen and oxygen. The content of nitrogen was very small. The C/H and C/O ratio of the lignin precursor reflects some degree of aromaticity and methoxy group in the lignin precursor [13–15]. In addition, the Lignin precursor could completely dissolve in water with pH value is 12 so that full contact could be maintained between the lignin molecule and alkali activators. The complete solubility of lignin in alkaline solution makes the activation facile and thorough.

2.2. Material preparations

Lignin precursor was dissolved in KOH aqueous at a mass ratio of 1:3, dried at 80°C for 12 h and activated at 800°C for 2 h under

nitrogen in a tube furnace. The obtained sample was washed with 1 M HCl solution and sufficient water repeatedly till a neutral pH was obtained. Finally, the samples were dried at 80°C for 24 h. For a better understanding of the pre-pyrolysis mechanism, the lignin precursor was firstly pyrolyzed at 600°C for 1 h and then as-obtained sample was activated treatment as mentioned before. Activation samples were named as LAC-D and LAC-P, representing directly activated sample and sample with pre-pyrolysis at 600°C , respectively. And pre-pyrolysis sample was named as L-P.

2.3. Material characterizations

The specific surface areas were calculated using the BET theory (TriStar 3000, GA). The total pore volumes (V_{tot}) were calculated from the amount of N_2 adsorbed at a relative pressure (P/P_0) of 0.99. The micropore volumes were calculated using the t-plot method and the surface areas and pore volumes of the mesopores were analyzed based on the Barrette-Joynere-Halenda (BJH) method. The pore size distributions were studied using the density functional theory (DFT) model. The macropore volumes (V_{mac}) and porosities were measured using an AutoPore IV 9510 mercury porosimetry analyzer from the Micrometrics Company. The morphologies of the LAC were observed by scanning electron microscope Phenom G2 pro and the magnification is $2000 \times$. An XRD (Rigaku D/Max 2500) was operated at 40 kV and 90 mA with Cu K α radiation ($\lambda = 0.154,056 \text{ nm}$) and the scan rate is $5^\circ/\text{min}$, angular ranger from 5° to 90° . Raman spectra were measured by a Renishaw MKI-2000 Raman microscope using an Ar ion laser (488 nm) as the excitation source. The surface of the samples was characterized by XPS using a PHI-1600ESCA electron system (America PE Company) with Al K α (1486.6 eV) radiation.

2.4. Electrochemical measurements

Electrodes were prepared by mixing LACs, polytetrafluoroethylene (PTFE) binder and carbon black with a mass ratio of 8:1:1. The mixture was homogenized by continuously stirring, rolled and pressed onto a nickel foam current collector. Disk-shaped electrodes were then cut out, dried and weighed. Finally, two-electrode symmetric supercapacitor cells were assembled with 6 M KOH as the electrolyte. Galvanostatic charge/discharge and cycle performance were tested using a Land Battery Tester (Wuhan, China) and an Arbin battery test instrument. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested on Princeton PARSTAT2273 electrochemical workstation (USA). The gravimetric capacitances were calculated according to $C_g = 2 I \Delta t / (m \Delta V)$, where I , Δt , ΔV and m are the discharge current (A), discharge time (s), voltage drop upon discharge excluding the IR drop (V), and the mass (g) of active materials. The energy density and average power density of the capacitor is calculated by $E = C_g \Delta V^2 / 2$ and $P = E / \Delta t$. The gravimetric capacitances were also calculated according to $C_g = (I dv) / (vmV)$, where I , v , V and m are the current (A), scan rate (mV/s), and the mass (g) of active materials. In addition, the gravimetric capacitances was calculated using

Table 1
Main properties of the Lignin precursor.

Raw material	Elemental analysis (wt%)					Ash (wt%)	Solubility	
	C	H	N	O ^a	C/H ^b			C/O ^c
Lignin precursor	60.93	5.77	0.73	31.64	0.88	2.57	0.17	Completely soluble in water, pH = 12

^a By difference.

^b Atomic ratio of C and H.

^c Atomic ratio of C and O.

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