REUTILIZATION OF HYDROLYZED LIGNIN RESIDUE INTO ULTRAHIGH SPECIFIC SURFACE AREA ACTIVATED CARBON FOR SUPERCAPACITOR

Ying Xu^{1, 2, 3,} *, Zifang Peng¹, Zhang Qi¹, Chenguang Wang¹, Longlong Ma¹

1 Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China; 2 Key Laboratory of Renewable Energy, Chinese Academy of Sciences, Guangzhou 510640, PR China; 3 Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, PR China Corresponding Author: <u>xuying@ms.giec.ac.cn</u>

ABSTRACT

The exploration of efficient utilization of lignin is very important and necessary for the applied biomass energy and sustainable development. In this work, hydrolyzed lignin residue, contenting more than 70% lignin, obtained from acid hydrolysis of sorghum straw was reused to synthesized ultrahigh surface area and hierarchical porous activated carbon for the first time. As-prepared nanomaterial (HLAC-1) presented unusual features such as unique interconnected porous structure, ultrahigh surface area (ca.2927 m²/g), large total volume (ca.1.65 cm^3/g) and a high graphitization degree. Furthermore, as the electrode material for supercapacitor, HLAC-1 also exhibited remarkably high capacitance (400 F/g at 0.5 A/g) and superior cycling stability (99.1% capacity retention after 20,000 cycles at 5 A/g) in 6M KOH aqueous electrolyte. A high energy density of 9.53 Wh/kg at a powder density of 53.22 W/kg (6.96 Wh/kg at a powder density of 2532.39 Wh/kg) have been achieved in KOH aqueous supercapacitors, indicating that the conversion of hydrolyzed lignin residue from activated carbon is very attractive and promising for the application in supercapacitor.

Keywords: hydrolyzed lignin, activated carbon, ultrahigh specific surface area, hierarchical porous structure, supercapacitor

NONMENCLATURE

Abbreviations

HL	Hydrolyzed lignin
HLAC	Hydrolyzed residue active carbon activated without activator
HLAC-1	Hydrolyzed residue active carbon activated by KOH
YP-50	A kind of commercial activated carbon

1. INTRODUCTION

Batteries keep various devices working throughout the day due to their high energy density but take hours to recharge when they run out of power. electrochemical capacitors also called supercapacitors are developed and used for rapid power delivery and recharging.

Porous carbon-based material is one of the most potential electrode active material owing to its light weight, large surface area, high chemical stability, diverse volume and pore structure. Among various carbon-based materials, natural biomass precursors, consist of cellulose, hemicellulose and lignin, are widely concerned as a potential energy application material due to its renewable, low cost and easy mass production. As second most abundant natural polymer after cellulose, lignin is the main byproduct of conventional pulp and paper industry and mostly consumed as a low-grade fuel in industrial burner or boiler.

Herein, we report the preparation of porous activated carbons using hydrolyzed lignin residue via KOH activation treatment. The as-synthesized hydrolyzed lignin active carbon possesses ultrahigh



Fig.1.SEM image of HL (a, b and c); HLAC, the samples activated without KOH (d, e and f); HLAC-1 (g, h and i)

specific surface area (up to 2927m2 g-1) and the hierarchical pore structure which enhanced the supercapacitance performance. The results indicated that HLAC-1 exhibited a high capacitance and outstanding cycling stability, demonstrating that hydrolyzed lignin porous carbon is a potential material for practical utilization in supercapacitors.

2. EXPERIMENT

2.1 Sample preparation

In a typical two-step activation process, 15g HL was carbonized at 400 °C for 1 h with a heating rate of 2 °C/min in a tube furnace under N₂ atmosphere. Subsequently, 1.5 g of as-prepared sample was dispersed in 30 mL KOH aqueous solution with a mass ratio of 1:3(solid product/KOH) and string for 8h and dried at 105 °C at vacuum overnight. Then the mixture was transferred to nickel crucibles and heated to 800 °C for 2 h with a heating rate of 5 °C /min, under the nitrogen atmosphere and cooled to room temperature naturally. Finally, the obtained black powder was further washed with 2.0M HCl aqueous solution and deionized water until neutral pH, followed by drying at 105 °C on vacuum overnight. The as-synthesized sample was denoted as hydrolyzed residue active carbon (HLAC-1). For the sake of comparision, 1.5g carbonized sample were dispersed with 30mL aqueous solution without KOH and treated with the same method. The sample was denoted as hydrolyzed residue active carbon (HLAC). The yield of carbonization and activation is 59 wt $\%\,$ and 23 wt %, respectively.

2.2 Characterization

The HL, HLAC and HLAC-1 were characterized by field emission electron microscope (FESEM), Raman Spectrometer, X-ray diffraction (XRD), Elementary Vario Micro Cube, N_2 adsorption-desorption isotherms (ASIQMO002-2 sorption analyzer). The surface area was calculated by Brunauer-Emmett-Teller (BET) theory. The pore size distribution was analyzed by Non-Local Density Functional Theory (NLDFT).

2.3 Electrochemical measurement

To evaluate the electrochemical performance of as synthesized activate carbon, the working electrode was prepared. Galvanostatic charge/discharge (GCD) and cyclic voltammetry (CV) were performed. The electrochemical impedance spectroscopy (EIS) was conducted on Im6ex electrochemical workstation (Zahnex Corp.). The frequency range of EIS is from 0.01 to 100 kHz with 5 mV amplitude.

3. RESULTS AND DISCUSSION

3.1 Morphological and structural characterizations

The morphology and microstructure were characterized by SEM. The HL presented a relatively uniform clavate shape which interconnect with each other. After activated without KOH(Fig.1d~f), the overall appearance of HLAC still maintain the clavate shape while which became smaller. However, it is worth pointing out that HLAC-1 exhibited a three-dimensional interconnected hierarchically structure. The randomly opened macropores with size range from a few hundred nanometers to several micrometers were well interconnected to each other. The magnified image clearly demonstrated that the numerous small-sized nanopores exist in the carbon skeletons of HLAC-1, confirming its highly developed porosity characteristic. Such interconnected open porous frameworks were beneficial since during the process of electrochemical tests, they were able to act as ion-buffering reservoirs and facilitate the diffusion rates.

The graphitization degree of HLAC-1 was characterized by XRD and Raman. The high graphitization



Fig.2 (a) XRD pattern and (b) Raman spectra; (c) N2 adsorption-desorption isotherm and (d) pore size distribution of HLAC-1 sample.

concentration in the HLAC-1 was beneficial for the application in supercapacitor since the electrochemical performance will be enhanced effectively. N₂ adsorption/desorption isotherms of HLAC-1 was carried out to examine the specific surface area and variation of pore size and pore distribution. As illustrated in Fig.2c, the HLAC-1 exhibited a typical type I adsorption-desorption isotherm with a typical microporous nature. Moreover, HLAC-1 exhibited a large BET surface area of 2927 m²/g, and its total pore volume was 1.65 cm³/g, in which 1.38 cm³/g was assigned to micropores.

3.2 Electrochemical Performance tested in a Three-Electrode System

To make a comparison and demonstrate the advantages of HLAC-1 sample in the application of supercapacitors, the electrochemical performance of a commercial activated carbon YP-50 was also investigated under the same experimental conditions.



Fig.3 Electrochemical performance of HLAC-1 and YP-50 measured in a three-electrode system in 6.0M KOH electrolyte. (a-b) Cycling voltammetry (CV) curves at different sweep rate of HLAC-1 and YP-50. (c-d) The galvanostatic charge-discharge (GCD)curves under various current densities ranging from 0.5 to 50 A g-1 of HLAC-1 and YP-50. (e)Comparison of EIS spectra (Nyquist plots) for HLAC-1 and YP-50. (f)Specific capacitance of HLAC-1 and YP-50 at different current density.

The CV curves of HLAC-1 showed a well symmetric rectangular shape with weakly broadened humps, which indicated that the dominant behavior of electrochemical double layer capacitance (EDLC) and limited pseudocapacitance from the oxygencontaining functional groups. In comparison, the CV curves of the YP-50 electrode were relatively smaller.

3.3 Electrochemical characterization of Symmetric Capacitors in a Two-Electrode System

To further investigating the electrochemical performance of the HLAC-1 sample, coin-type twoelectrode system in 6M KOH aqueous solution measurement was conducted. CV curves (Fig.4.a) scanning from 5 to 200 mV/s exhibited rectangular shape even at the high scan rate of 200 mV/s indicating fast ion transfer process and excellent capacitive behaviors. GCD profile (Fig.4.b) display nearly linear and relatively symmetrical, confirming that HLAC-1 electrode had excellent electrochemical reversibility and columbic efficiency.



Fig.4 Electrochemical performance of the HLAC-1 sample in a two-electrode system using 6M KOH aqueous solution as electrolytes. (a)CV curves at various scan rates. (b)GCD curves under different current densities. (c) Specific capacitance as a function of current densities. (d)
Capacitance retention of HLAC-1 in KOH electrolyte after 20,000 cycles at 5 A g-1.

4. CONCLUSIONS

In summary, a new kind of hierarchical porous activated carbon material with ultrahigh surface area of 2927 m^2/g has been synthesized from HL residue. Remarkably, the activated carbon activated by KOH exhibited outstanding electrochemical performance in the application in aqueous supercapacitor (high specific capacitance of 400F/g at 0.5A/g, excellent cycling stability of 99.1% after 20,000 cycles and etc), superior than that of the commercial YP-50 activated carbon. In particular, hydrolyzed lignin residue for the usage as advanced material of supercapacitor achieve full utilization of biomass components, which is consistent with the idea of renewable economy and sustainable development, indicating its significant potential in practical applications, such as catalysis, adsorption and other energy storage device.

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