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Engineering biorefinery residues from loblolly pine for supercapacitor applications

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ABSTRACT

Recycling agricultural waste biomass into high-value-added products is of great importance to offset the cost of biofuel production. Here, we make biochar-based activated carbons (BACs) from loblolly pine chips via different carbonization recipes and chemical activations. BACs were then assembled into electrochemical double-layer capacitors (EDLCs) as electrode materials. Surprisingly, pyrolysis at lower temperatures (300 °C and 350 °C) rendered better electrochemical performance of BACs than those done at higher temperatures (500 °C and 700 °C). This is mainly due to the large surface area and high pore volume generated at the lower temperatures. Among all the pyrolysis recipes, flash pyrolysis at 300 °C produced the BAC with the highest specific capacitance (74 F g^{-1} at 20 mV s^{-1}), exceeding the specific capacitance of commercial activated carbon (NORIT®) by 45%. This report demonstrates the great potential of our refinery recipe to engineer BACs from the sustainable, affordable, and abundant natural wastes for energy-storage applications, which opens the door for a group of biorefinery residues for value-added applications.

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1. Introduction

In recent years, extensive research has been reported on sustainable processing of low-value biomaterials for energy-storage applications. For example, banana peels [1] and ambient air-derived carbon dioxide [2,3] have been converted to carbon nanostructures for Li-ion and Na-ion battery applications; carbon hybrids derived from peanut shells have been applied in Na-ion capacitors with energy-power performance better than that of Li-ion batteries [4]. Lignocellulosic biomass from agricultural and forest wastes is abundant and renewable [5]. They can be transformed into hydrocarbon fuel through pyrolysis via C_5 and C_6 sugar intermediates [6]. During the conversion process, biochar is generated as a byproduct of pyrolysis, and its wide-spread application into new products is highly desired in order to lower the overall cost of the biofuel [7]. Biochar combustion to generate steam and power is a viable option, but the least economic route for

utilization (~$100 per dry ton). Therefore, upgrading biochar into high value products is critical to improving the overall economic feasibility. In recent years, biochar originating from agricultural biomass waste, such as apricot shells [8], sunflower seed shells [9], rice husks [10] etc., have been proven to be promising in producing activated carbon (AC) for application in Electrochemical Double-layer Capacitors (EDLCs). The production of biochar-based activated carbon (BAC) from biomass usually includes carbonization and activation [11]. The biochar production process (carbonization) requires a hot sealed reactor with little or no available oxygen (O_2). These reactors can be accomplished at low cost without negative environmental effects due to their nontoxic and recyclable nature making this a sustainable option [12]. Activation is a process of converting carbonaceous biochar into AC with optimized surface area and porous structure [7,11]. Chemical activation could increase the Brunauer-Emmett-Teller (BET) surface area of the carbon materials up to 1500 m^2/g [13], comparable to that of the commercial AC, while still retaining an electrical conductivity of ~2.3 S/cm, higher than that of commercially-used AC. The carbonization conditions, such as the temperature and the ramping rate (flash or slow pyrolysis), have significant impact on the microstructures of biochar samples, resulting in large discrepancies in their

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electrochemical performance made with different recipes [8].

Carbon-based materials have been widely used in EDLCs because of several notable advantages, including large abundance, versatile existing forms (powders, fibers, felts etc.) [14], high surface areas, good electrical conductivity, and good stability in various electrolytes. Although a wide range of nanostructured carbons, such as carbon nanotubes [15], carbide-derived carbons [16], and graphene derivatives [17], have been prepared and evaluated as supercapacitor electrode materials, their relatively high cost and tendency to produce secondary environmental pollution have hindered their practical applications in EDLCs [12,18]. Therefore, developing low-cost carbon with minimal environmental impact and good performance is highly desirable throughout the energy-storage industry.

EDLCs are energy-storage devices that possess quick charge/discharge capability and long cycle life, arousing considerable interest in applications such as electric automobiles, digital communication systems, and peak-power required instruments (elevators and cranes) etc [19–21]. EDLCs store energy via reversible ion adsorption on the electrode-electrolyte interfaces [22]. Thus, electrode materials, the nature of electrolyte and electrode-electrolyte interfaces will all have significant influence on EDLC performance. Among those, the electrode plays the most important role in determining the energy and power densities of an EDLC [18]. Large specific capacitance, good rate capability and high cyclic stability are the most crucial criteria for an EDLC electrode [22]. Correspondingly, the surface area, porous structure, electronic conductivity and chemical stability are the most relevant properties of the electrode materials. In addition, the cost and environmental impacts should also be taken into account [12,22]. Biochar as the by-product of pyrolysis technology used for biofuel and bioenergy production, is within the carbon cycling loop. Recycling biochar is a novel approach to sink atmospheric carbon dioxide into terrestrial ecosystems [23]. These benefits make large scale application of biochar possible with minimal environmental effects.

Recently, the preparation and characterization of biochar-based activated-carbon electrodes have attracted much attention. AC made from cotton stalks and activated by phosphoric acid exhibited a specific capacitance of 114 F g^{-1} [24]. Oil-palm empty-fruit bunches treated with KOH showed a capacitance of 150 F g^{-1} [5]. Coffee endocarp generated biochar with KOH activation had a specific capacitance of 69 F g^{-1} [25]. Based on these studies, it could be established that the surface area, pore structures, conductivity and electrochemical performance largely depend on the physiochemical properties of the precursor material as well as the activation process. In comparison with KOH, NaOH is a better choice as the activation agent because of its lower cost and lower corrosiveness [26]. In addition, the physiochemical properties of precursor materials are strongly dependent on the nature of feedstock and pyrolysis conditions, especially the temperature and the ramping rate [7]. However, as far as we know, a thorough study on different pyrolysis conditions and the resulted electrochemical behaviors is currently missing.

Loblolly pine is the most important, widely cultivated and productive timber species in the southern United States [27]. Compared to other hardwood and softwood, loblolly pines generally grow faster [28]. Their established industrial chain together with high yields make them a good candidate for the biomass feedstock. Loblolly pine has already been made into biochar and value-added ACs used in the sorption of phenanthrene [7]. However, there is no study on electrochemical performance of the AC originating from loblolly pines.

In this paper, we prepared biochar-based activated carbon (BAC) powder by carbonization of loblolly pines with different pyrolysis temperatures and pyrolysis rates (flash pyrolysis and slow pyrolysis). Our biochar product was later activated with NaOH to generate the desired porous structures. Supercapacitor electrodes were developed with the BAC powders and no binder was used in our electrodes. The microstructure and electrochemical performance of BAC made from different pyrolysis conditions have been investigated extensively. For comparison, a commercial AC was also investigated in this work. By optimizing the pyrolysis temperature and rate, BAC made from flash pyrolysis under 300 °C exceeded specific capacitance of the commercial AC by 45%. The systematic investigation of pyrolysis conditions will help in the development of BAC and their application in electrochemical supercapacitors.

2. Experimental section

2.1. Preparation of BAC

Loblolly pine derived BAC was prepared by a two-step process which included carbonization and chemical activation. Loblolly pine woodchips approximately 3–5 cm in length were milled into 20-mesh size particles using laboratory Wiley Mill and air dried for 24 h. Further carbonization was done by using OTF-1200X quartz tube furnace (MTI Corporation, Richmond, CA, USA). Two heating rates (flash heating, 5 °C/min) and four carbonization temperatures (300, 350, 500, and 700 °C) were chosen to produce biochar samples with different physical and chemical properties. A mass of 7–8 g of milled loblolly pine was loaded onto an aluminum crucible which was then inserted into the quartz tube. A constant stream (1 L/min) of nitrogen gas was purged and each sample remained in the furnace for 15 min after reaching the target carbonization temperature. The resulting biochar was pulled out of the furnace and quenched at room temperature under nitrogen flow.

To produce BAC, sodium hydroxide impregnation method was used. Biochar was stirred in 4 M sodium hydroxide solution for 2 h (3 g of biochar/40 ml NaOH). Impregnated biochar was collected by filtration and oven dried at 110 °C overnight. The oven dried sample was transferred into an aluminum crucible and the crucible was loaded in the quartz tube. A constant stream (2 L/min) of nitrogen gas was purged into the tube. The furnace was heated from room temperature to 800 °C at 3 °C/min of heating rate. The sample remained in the 800 °C furnace for 2 h. Following activation, the sample was cooled to room temperature under nitrogen flow. The BAC was washed with 200 ml of 0.1 M hydrochloric acid solution and 2 L of deionized water, and then dried at 110 °C. The nomenclature of flash heating BAC is Nxxx-F-AC and 5 °C/min heating BAC is Nxxx-S-AC, where xxx indicates the carbonization temperature.

2.2. Physical-property characterization

Scanning electron microscopic (SEM) images of BAC were taken by Verios 460 L Field Emission Scanning Electron Microscope (FEI, Hillsboro, OR, USA). BET surface area and Barrett-Joyner-Halenda (BJH) pore volume of BAC samples were analyzed with Gemini VII 2390 surface area analyzer (Micromeritics, Norcross, GA, USA). A 0.15–0.20 g sample of BAC was loaded in the glass tube and degassed with 220 °C nitrogen gas for 2 h. Multipoint BET surface area was calculated from the linear relative pressure regime of $0.05 < P/P0 < 0.30$. Total pore volume was calculated at $P/P0 = 0.98$. BJH adsorption log differential pore volume was plotted to compare different pore structures in BAC samples.

Elemental carbon, hydrogen, and nitrogen contents of BAC samples were analyzed by Perkin Elmer 2400 Series II elemental analyzer (PerkinElmer, Waltham, MA). Oxygen content was calculated by subtracting CHN compositions from 100. X-ray Photoelectron Spectroscopy (XPS) Analysis was conducted by SPECS XPS/UVS System with PHOIBOS 150 Analyzer (SPECS Surface Nano