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Preliminary investigation of electrical conductivity of monolithic biochar

Randeep S. Gabhi, Donald W. Kirk, Charles Q. Jia*

Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, ON, M5S 3E5, Canada

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ABSTRACT

Monolithic biochar is explored as electrode material in supercapacitor – a fast-charging, long-lasting energy storage device. Electrical conductivity of electrode is critical to supercapacitor's performance. Traditionally, biochar is used as a solid fuel for combustion where electrical conductivity is largely irrelevant and ignored. This work explores electrical conductivity of monolithic biochar and elucidates its dependence on micro and macro structures of biochar. Electrical conductivity of biochar was found to be highly dependent on its degree of carbonization. Bulk conductivity of biochar can increase by over six orders of magnitudes when its carbon content changes from 86.8 to 93.7 wt%. Transmission electronic microscope and x-ray diffraction analyses revealed the presence of graphite nanocrystals (~3 nm) and the growth of biochar crystallinity after heat treatment at 950 °C. The highest skeletal conductivity of carbon was 343.2 S/m, found in a heat-treated sugar maple biochar with 96.2 wt% of carbon. It is higher than that of graphite single crystal in direction perpendicular to graphene plane (333.3 S/m). Moreover, it was observed conductivity of monolithic biochar increased with compressive loading and dropped to the pre-compression level when the loading was released - a new phenomenon termed "elastic behavior of electrical conductivity of biochar".

1. Introduction

Lignocellulosic biomass is plant-based material which captures and stores atmospheric carbon dioxide via photosynthesis. This biomass is an emerging source of carbon-neutral fuel [1]. Dry lignocellulosic biomass, such as wood and agricultural wastes, typically consists of 50 wt% of carbon. Carbon in biomass can be retained via carbonization or pyrolysis by which biochar, a carbon-rich product, is manufactured [2,3]. Pyrolysis processes can be slow or fast depending on the feed and the desired quality of biochar. Microwave pyrolysis is new way used to produce biochar [4–8]. Biochar structures range from graphite-like carbon to high molecular weight poly-aromatic hydrocarbon rings [9–11]. Biochar is inherently porous due to its precursor structure. Highly carbonized biochar (>90 wt% of carbon) is chemically stable under ambient conditions. Production and utilization of chemically stable biochar can be considered as a mechanism of carbon capture and storage – an overall carbon-negative process that removes carbon from the carbon cycle. In one application, biochars have been shown to improve soil fertility and crop performance by balancing the pH of acidic soils [3] and increasing microbial activity [12]. In another application, owning to its chemical stability and electrical conductivity, biochar has been explored as electrode materials in energy storage and in electrokinetic soil remediation [2].

More specifically, traditional methods to store electrical energy include batteries and dielectric capacitors [13]. Electrochemical double layer capacitors (EDLCs), or supercapacitors, are energy storage devices that have properties shared by both batteries and capacitors. Batteries can store high energy but charge or discharge slowly, whereas capacitors can charge nearly instantaneously but have less storage capacity. Supercapacitors. In this work we focus on the electrical conductivity properties for supercapacitors. In EDLC, electrical conductivity of its electrode material is critical to its performance and electrodes have high electrical conductivity and high surface area. In general, conductivity is a measure of the rate of charge transfer through the device. Carbon electrode materials currently under study include graphene and carbon nanotubes which possess high electrical conductivity, high surface area and high mechanical strength accentuated with good cycling stability [14–17]. However, these materials face many challenges associated

* Corresponding author.
E-mail address: cq.jia@utoronto.ca (C.Q. Jia).

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with economics and scale-up.

Although there has been some biochar conductivity data in literature, it is limited to powdered porous biochars [18–21]. This work focuses specifically on the electrical conductivity of monolithic biochar from wood – a topic that has not been systematically explored. The goal is to reveal its structure and property relationship to answer the question about what controls the conductivity of biochar. The new knowledge gained from this study will guide the design and manufacture of highly-conductive porous biochar for energy and environmental applications.

2. Experimental

2.1. Preparation and characterization of biochar samples

2.1.1. Biochar sample preparation

Biochar samples for conductivity measurements were prepared from commercial charcoal products obtained from three different suppliers. As expected, commercial charcoal products were highly variable in their appearance and carbon content. Given the heterogeneous nature of commercial products, charcoal pieces were screened and selected using a visual inspection. The focus was the blackness of the sample and the continuity of the surface, i.e., no visible cracks. The biochar was produced commercially from three types of trees (sugar maple, oak and hickory) a grass and bamboo.

Cylindrical biochar samples were made from large chunks of charcoal using a 5/8″ core drill bit. The cylindrical cores were reduced in length using sandpaper from grade 60 to 400 in order to meet ASTM C695-2010 specifications: an aspect ratio between 1.9 and 2.1 of length to diameter (width). The resulting length and diameter of the samples were approximately 26 mm and 13 mm, respectively. The ends of the cylinders were levelled using a bubble level and a right angle vice.

2.1.2. Elemental analysis

Elemental analysis was carried out using a CE440 Elemental Analyzer, to measure carbon, hydrogen, oxygen and nitrogen contents of biochar through combustion. Carbon content is the most important value, as it is a measure of the degree of carbonization. Carbon content of biochar is expected to be much greater than 50 wt% which is the typical value of dry wood. 1–2 mg of each sample were analyzed and results for each sample were run in triplicate and average values with standard deviation are reported for CHN content.

2.1.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out using a TA Instruments Inc. TGA Q500 Evolved Gas Analysis furnace. The furnace provides a controlled volume where samples are heated at designated heating rates under argon. Argon gas is used to provide inert atmosphere and prevent combustion of the samples. The sample was heated from room temperature to 100 °C by ramping at 25 °C/min, then held at 100 °C for 10 min, then heated to 800 °C at 20 °C/min and finally held at 800 °C for 10 min before stopping. The data was processed to create TGA and DTG curves, which are used to evaluate the mass-loss and its dependence on temperature.

2.1.4. X-ray diffraction

X-ray Diffraction (XRD) analysis was performed using a Rigaku MiniFlex 600 system equipped with 2.0 kW Cu X-ray tube with a graphite monochromator. Scans were carried out over the 2θ range of 10–50°, using a step size of 0.02° and scan speed of 2 s/step. Samples were crushed using mortar and pestle and meshed to achieve particle size less than 50 μm. The amount of sample used was 1–2 mg, enough to cover the XRD grid. Particle size was maintained constant for all samples to maintain uniformity. XRD analyzes biochar to detect {002} and {100} peaks of graphite crystals at 25° and 41.6°, respectively.

2.1.5. Transmission electron microscopy

Transmission electron microscopy (TEM) was carried out on a Hitachi 300 kV HF-3300 TEM/STEM with cold field emission gun technology, at 100 kV electron beam to locate crystals in biochar samples. Samples were crushed using a mortar and pestle, to achieve biochar particles thinner than 100 nm. Crushed biochar was dispersed in a small amount of isopropanol. The dispersed samples were transferred onto the TEM sample grid using a fine point tweezer. The loaded TEM sample grid was inspected under an optical microscope to ensure the presence of thin biochar particles.

2.2. Electrical conductivity measurements

The electrical conductivity was measured using two different methods – one with and one without compression. Fig. 1 shows the set-up that allows compression loading on biochar samples and the study of the dependence of conductivity on compression. The compression machine used was Sintech 20 with a loading head of 20,000 lb. Aluminum foil was used to connect biochar to a multimeter and insulated from the equipment using two pieces of 1″ Plexi glass which were attached to the loading and bearing heads, respectively. The loading rate was set to 1 mm/min, to ensure sufficient time to record conductivity against loading, and in accordance with ASTM standard C695-2010.

A Hewlett Packard 34401 A multimeter was used to measure the resistance across the biochar, which was converted to conductivity for samples of known dimension. The electrical resistance value was recorded only after a stable reading was achieved with a good contact between the aluminum foil and the biochar sample. The equipment recorded the pressure exerted on the sample against the change in height of the sample and evaluated the peak stress and the ultimate stress. A stopwatch was used to measure the time period simultaneously with compression to correlate compression measurements with resistance.

In order to determine electrical conductivity of biochar, contact resistance must be eliminated from the measured total resistance. It is achieved by measuring the resistance of samples of different sample lengths (typically 2–10 mm) and by applying a graphite

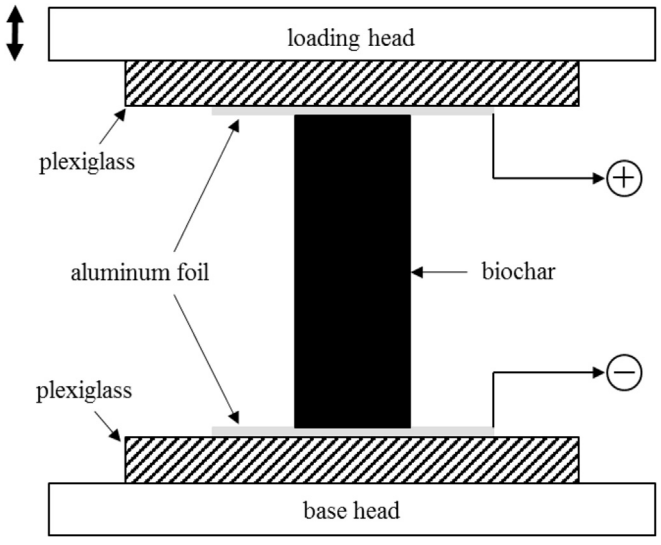

Fig. 1. Setup for compression test to measure conductivity.