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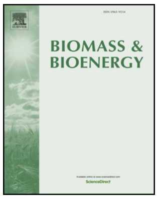

Research paper

Dependence of supercapacitor performance on macro-structure of monolithic biochar electrodes

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ABSTRACT

Large-scale applications of recalcitrant biochar produced from photosynthetic biomass are considered a "carbon-negative" measure that can help reduce the growing stockpile of atmospheric carbon. One such application is to use biochar as the electrode material in supercapacitors, a fast-charging and long-lasting electrical energy storage device. To facilitate devices' performance, commercial supercapacitor electrodes typically take the form of thin films (~ 50 μm) made of activated carbon powder and a binder. Consequently, the fraction of active electrode material is small, as is its energy density. While thickening electrodes increases the fraction of active material, it also raises the resistance to electron and ion transport within the powder-based electrode. It is hypothesized that the use of monolithic biochar will enable thicker electrodes with adequate device performance. In this work, supercapacitor cells were constructed with monolithic biochar electrodes of different orientations and thickness. The specific capacitance and its dependence on current density were measured with a set of electrochemical methods and used to evaluate the performance of these cells. These experiments revealed that the inherent macro-structure of biochar plays a significant role in determining the performance of monolithic biochar electrodes. The dimension of structural features, such as the length of tracheids, can dictate the depth of electrolyte penetration. It is demonstrated that the proper design and manufacturing of monolithic biochar can extend the effective thickness of supercapacitor electrode to ~ 1 cm, establishing the feasibility of increasing energy density of supercapacitors by using thick, monolithic biochar.

1. Introduction

Biochars are high carbon content materials that are the result of thermally decomposing biomass [1–5]. Traditionally used as solid fuel or powder adsorbent [6–12], biochar is not commonly considered as a material suitable for building a high-performance device or a system. Applications that utilize biochar in large scales are of particular interest in the research community because it can be used to isolate and remove carbon from the carbon cycle [13–16].

Supercapacitors are a class of fast-charging, long-lasting electrical energy storage devices that rely on the formation of an electrical double layer on the internal surface of porous electrode material [17,18]. Supercapacitors have a wide range of applications, ranging from commercial electronics to renewable energy harvesting [19–21]. Commercial supercapacitor devices are composed of many cylindrical cells [22,23] in which layers of conductive foil (~ 25 μm thick) encase activated carbon powder films, (5–50 μm thick) [24]. Excluding the supporting equipment (e.g. cell mounts, connections), the active electrode material composes at most 50 vol % of a device. The low volume fraction of active electrode material limits the overall energy density and makes the device prohibitively costly for large-scale applications, such as an electrical buffer in electrical infrastructure. In addition to commercial devices, supercapacitor literature has been focused on improving the performance of carbon powders films [25]. In contrast, a direct solution to the problem of device scaling is to make the electrodes much thicker than the current collector (the conductive foil).

Monolithic electrodes are a means to achieve much thicker electrodes as they have no binder, a continuous and rigid solid structure, and a continuous pore structure. Treated and untreated biochar powders have been studied [26]. However, there are a limited number of publications that study biochar monoliths [27–29]. Those that are studied look to use wood-derived biochars to take advantage of the interconnected wood structures that exist throughout the trunk of a tree [30]. In addition to the macroporous structure, monolithic biochar is electrically conductive [31].

In literature, small monolithic electrodes (1 × 1 × 0.5 mm, 1 mg in mass) have been made from maple wood-derived biochar. The specific capacitance is similar to that of a 200 μm thin film made of biochar

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powder [28]. Using disk-shaped monolithic electrode with the geometric area of 18 mm^2 and thickness of 0.7 mm, the same study reported over a 50% loss in specific capacitance relative to the other two electrodes. Another study of similarly sized electrodes using an organic electrolyte can be found in Ref. [29]. One other study of note [27], tested 1 cm × 1 cm x 1 mm electrodes that outperformed the disc electrode of [28].

This study explores monolithic biochar electrodes that are much larger that each of the cited studies (2–10 mm thick with 25–100 mm^2 cross-sections), with a focus on the role that the macro-structures in biochar play in supercapacitor performance. This role is assessed by fabricating and testing the electrodes in various sizes, geometries and orientations and comparing it to corresponding changes to the magnitude of specific capacitance. The electrochemical impedance spectroscopy study of this work can be found in Ref. [32].

2. Experimental

2.1. Biochar material

Commercially produced biochar from hardwood was purchased from Basques Hardwood Charcoal (Quebec, Canada). Although the exact species is unknown, the conversion of wood to commercial biochar is typically preceded by a fast drying process, and uses carbonization [33]. The biochar pieces were heterogeneous in the degree of carbonization, having surfaces that vary from brown and non-reflective to black and glassy with carbon content varying from 85 to 95 wt%. Electrical conductivity of the biochar samples varied across orders several of magnitude, where samples with the closest to the highest value (400 S m^{-1}) were used [31]. Large pieces with the highest electrical conductivity were selected to create electrodes that were free of visible cracks.

The pieces used in this study were found to be micro-porous with a total surface area around ~600 m^2 g^{-1} using the method described in Ref. [34]. Their pore structure was studied using a Hitachi 3500 variable pressure scanning electron microscope (VP-SEM) at the Ontario Centre for the Characterisation of Advanced Materials at the University of Toronto (OCCAM). The acceleration voltage used was 5 kV.

2.2. Device assembly and electrode fabrication

A schematic of the setup used to test biochar electrodes and the notations describing electrode orientation are illustrated in Fig. 1. In the centre of the diagram is a supercapacitor cell, where two monolithic biochar electrodes are placed between two nickel mesh current collectors, and separated by a fibrous polysulfone separator. The cell is submerged in 4 M KOH electrolyte, and then sealed within a PTFE jar. An inlet and outlet in the lid are used to maintain an inert headspace with a grade 5.0 nitrogen gas, preventing the neutralization of the electrolyte.

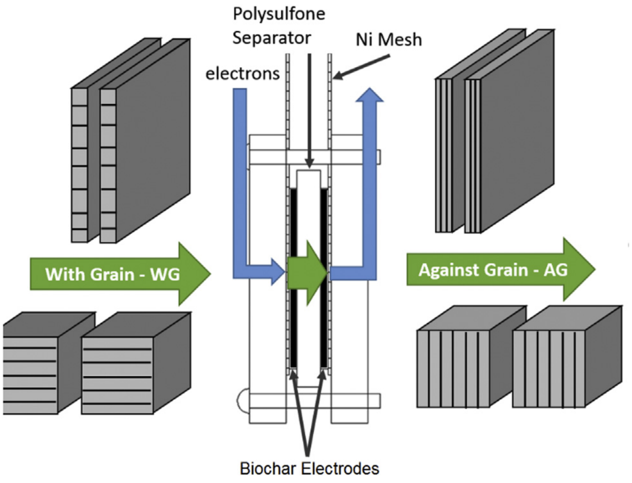

Fig. 1. Supercapacitor cell construction and biochar electrode orientation; Top left and right are depictions of the WG and AG electrodes; Bottom left and right are depictions of cubes in either direction.

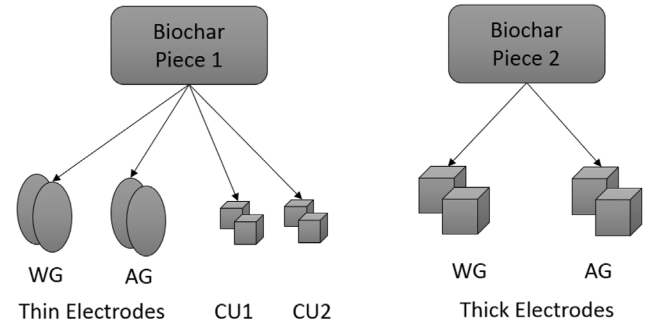

Fig. 2. A schematic summary of the electrode geometries and relative sizes used in this study. The Thin electrodes had a cross-section of ~1 cm^2, that of cubes ~0.25 cm^2, and that of the Thick electrodes ~1 cm^2.

The selected pieces of the biochar were used to form three electrode pairs of different geometries and orientations. The orientation was defined with respect to the direction of wood grain – the axial direction. Two electrode orientations illustrated in Fig. 1 are relative to the direction of net electron flow: with grain (WG) if electron flow is parallel to the axial direction, and against grain (AG) if electron flow is perpendicular to the axial direction.

The first two sets of electrodes were made from a single piece of biochar (Fig. 2). The first set consists of two pairs of thin disks with a face of ~120 mm^2 in area and 1.4 mm thick, each fabricated with the "with grain" and "against grain" orientations in mind (Fig. 1). They are denoted "Thin WG" and "Thin AG" electrodes, respectively. The second set is made from the same biochar piece: two pairs of cube shaped electrodes (~5 × 5 × 5 mm), denoted as CU1 electrodes and CU2 electrodes, respectively. The third set of electrodes, made from a different piece of biochar, was fabricated into two pairs of large cubes (~10 × 10 × 10 mm), each to have a fixed orientation. They were denoted Thick AG and Thick WG according to the direction they were kept in the cell.

2.3. Quantification of supercapacitor electrode performance

Two devices (Metrohm PGSTAT 302 N and Solartron 1250 B PGSTAT) were used to collect data for quantifying the performance of supercapacitor cell. Constant current measurements (i.e. galvanostatic cycle or GC) were conducted to determine capacitance and resistance of a cell. Prior to data collection, the cell was conditioned by cycling for ~60 h. The device capacitance was normalized to the mass of both electrodes and presented as specific capacitance in F·g^{-1}. Current density is extensively used in electrochemistry to normalize current to the geometric cross-sectional area of an electrode. As a fundamental study of electrode material, the current here was normalized to the mass of the electrode. This normalized current is referred to as specific current in mA·g^{-1}. Most data in this study is presented as plots of specific capacitance (F·g^{-1}) and specific current (mA·g^{-1}). Detailed procedure of measurements can be found in literature [35].

3. Results and discussion

3.1. Morphological features of hardwood-derived monolithic biochar

Figs. 3 and 4 are SEM images of the thin with-grain (WG) and against-grain (AG) electrodes, respectively. Fig. 3 is the axial view of