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Full paper

High-frequency electrochemical capacitors based on plasma pyrolyzed bacterial cellulose aerogel for current ripple filtering and pulse energy storage

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ABSTRACT

There are great needs in developing compact-size kilohertz (kHz) high-frequency (HF) electrochemical capacitors (ECs) for ripple current filtering and environmental vibration energy harvesting. However, the previously demonstrated electrodes are generally limited to a very small areal capacitance density at 120 Hz due to sub-μm thick electrode used for meeting frequency requirement, which renders them unsuitable for practical ECs. Here, using crosslinked carbon nanofiber aerogel, derived from rapid microwave plasma pyrolysis of bacterial cellulose that was synthesized in a fermentation process, we demonstrated kHz HF-ECs with areal capacitance density as high as 4.5 mF cm^{-2} at 120 Hz in an aqueous electrolyte. The cruciality of plasma pyrolysis on high frequency response of the derived carbon nanofiber aerogel was discussed. The electrode performance in an organic electrolyte was further studied for operation in a large potential window of more than 3 V. Using such kHz HF-ECs, we further demonstrated their applications in rapid pulse energy storage for vibrational energy harvesting, as well as in ripple current filtering for AC/DC conversion. The promising results suggest this technology has great potential for developing practical compact HF-ECs in substitution of electrolytic capacitors for several crucial applications.

1. Introduction

Electrochemical capacitors (ECs) are being widely investigated to increase their energy density, to function as independent energy source or in supplement with the low power batteries. As energy sources, ECs have a charge and discharge rate (frequency) limited up to approximately 1 s (1 Hz). In other words, they work under direct current (DC). They will behave more like a resistor but not a capacitor at higher frequencies. Therefore, these conventional ECs cannot play the roles of conventional electrolytic capacitors that work at much higher frequencies for ripple current filtering [1,2], decoupling, high-frequency pulse energy storage, and other functions.

A huge performance gap exists between conventional ECs and electrolytic capacitors [3]. ECs provide much larger capacitance density than electrolytic capacitors, but the latter can respond at tens of kilohertz (kHz) frequencies. Since electrolytic capacitors are commonly used for ripple current filtering in AC/DC converters and DC links, while their large size is becoming a limiting factor in downscaling the circuit design, there are great needs and interests in developing high-frequency (HF) ECs for filtering applications. For 60 Hz line-frequency, considering the harmonic frequencies after rectification, such HF-ECs should respond at hundreds to kilohertz range. In another frontier, environmental energy harvesting through piezoelectric- or triboelectric-generator is promising for self-powered autonomous sensors and internet of things (IOT) technology, while the environmental mechanical energy sources and hence the outputs from the micro-generators are typically pulsed currents with tens or hundreds Hz [4–6]. They also require kHz HF-ECs to efficiently store the harvested energy.

To evaluate the response frequency of a capacitor, the characteristic frequency f_0 when the impedance phase angle reaches $-45°$ is commonly used, which defines the boundary between capacitance dominance and resistance dominance. Of the two categories of ECs, pseudocapacitors are intrinsically slow even though fast pseudocapacitors were reported [7,8], while electric double layer capacitors (EDLCs) in principle are capable of charging and discharging within milliseconds, promising for kHz HF-ECs [9–13]. This strongly depends on the

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nanostructure of electrodes, conductivity of the electrode material and the choice of electrolyte [3,14]. In terms of the electrode nanostructure, reduction of porosity and electrode thickness [15,16] to accelerate electrolyte ions transport is the key for high-frequency response. However, this diminishes the achievable capacitance.

Towards high-frequency response [3] by partially sacrificing capacitance, vertically-oriented graphene (VOG) [1,9,13] and carbon nanotube (CNT) ultra-thin film [11,17] have been widely studied. Since very thin (~ 1–0.1 μm) "active" materials were used, they provided a very limited areal capacitance density. For conventional sandwich-type cell configuration, practical consideration requires a fairly thick active material layer to minimize the mass and volume penalties associated with the inactive components that include separators, electrolytes, current collectors, and packaging. This is particularly true when multiple cells have to be serially packed together for a high voltage rating [18]. Thick films or 3D structures, including reduced graphene oxide (rGO) aerogel [2], carbon black/VOG [18], edge-oriented graphene (EOG) [10,12], holey rGO film [19], CMK3/CNT composite [20], and others [21] were therefore reported with larger areal capacitance density. Further improving the areal capacitance to a new level is in demand for compact HF-ECs. In addition, most demonstrations are based on aqueous electrolytes due to their high ionic conductivity. However, with a limited potential window (< 1 V), aqueous electrolyte restricts the volumetric capacitance density in a high-voltage EC since more units are required to be connected in series to obtain a given rating voltage. In this regard, an organic electrolyte with potential window up to ~ 3 V has its merit [20,22,23].

Here we report crosslinked carbon nanofiber aerogel derived from pyrolysis of bacterial cellulose (BC) cultivated using Kombucha strains, as freestanding electrodes for kHz HF-ECs with much larger areal capacitance density. The whole process is illustrated in Fig. 1a. The carbonized BC (CBC) aerogel electrode was produced by pyrolysis of BC aerogel in microwave plasma of hydrogen and methane (CH_4) mixture for only 15 min. The pyrolyzed product, with a suitable porous structure, was directly applied as electrodes to assemble coin cells without any further processing. Compared to other reports involving complex steps in preparation of nanostructured electrodes [24–27], the fabrication route adopted here is simple and straightforward, and the produced CBC electrodes were demonstrated to be very suitable for HF-ECs. In particular, CBC electrodes in an aqueous electrolyte exhibited f_0 = 3.3 kHz and C_A^{120} = 2.98 mF cm^{-2} or f_0 = 1.3 kHz and C_A^{120} = 4.50 mF cm^{-2} for two different thickness, where f_0 is the characteristic frequency when the phase reaches – 45° and C_A^{120} is the areal capacitance density at 120 Hz. Our results are extraordinary considering that most publications report a limited C_A^{120} values, resulting in a packaged HF-EC without significant preponderance in term of volumetric density when comparing to electrolytic capacitors [3]. The pyrolysis conditions on high frequency response of the CBC aerogel was discussed. It deserves to emphasize that pyrolyzed bacterial cellulose through thermal process was reported previously as electrodes for ECs [25,28–32]. However, those ECs are still conventional slow ECs due to a different pyrolysis process used, as will be discussed by comparing the different pyrolysis processes. The operating voltage range of our CBC based HF-ECs was further expanded to 3 V by utilizing an organic electrolyte for practical applications. With the assembled HF-ECs, their applications for ripple current filtering and pulse energy harvesting and storage were further demonstrated.

2. Results and discussion

2.1. BC and CBC material studies

Carbon nanostructures derived from natural biomass are being studied as renewable resources for electrode applications. Cellulose microfibrils secreted by bacteria are of particular appeal [33,34]. They are long hydrocarbon polymer chains with a diameter of 1.78 nm, which form 3–4 nm bundles through hydrogen bonding, and then into nanoribbons, and further crosslink into a three-dimensional web structure [35].

In our study, BC pellicles were produced in a fermentation process using Kombucha strains [36], the method used for production of Kombucha tea, as detailed in the Supplementary information (SI). One BC pellicle cultivated in a container is shown in Fig. S1a in the Supplementary information. A piece of BC hydrogel after cleaning with NaOH and NaOCl solution and DI water to eliminate bacterial cells, BC aerogel obtained after freeze-drying, and the corresponding CBC after rapid plasma pyrolysis are also shown to indicate their dimensional change (Fig. S1b–d). The BC aerogel has a mass of less than 1% of its hydrogel counterpart. Scanning electron microscopy (SEM) image reveals the three-dimensional web structure of BC aerogel (Figs. 1b and S2a), while the crosslink between nanofibers or branch structure is noted in the transmission electron microscopy (TEM) image (Figs. 1c and S2b).

As a carbon precursor, BC is preferred over other natural celluloses due to smaller fiber size (around 10–50 nm) and higher degree of crystallinity and purity. The x-ray diffraction (XRD) pattern (Fig. 1h) indicates good crystallization of the cellulose. According to the cellulose I_α indexation, the three peaks corresponding to 2θ diffraction angles of 14.45, 16.75 and 22.75° are indexed to (100), (010) and (110) crystallographic planes [37]. The high-resolution TEM image (Fig. 1d) shows the (110) lattice planes with a plane spacing of 0.38 nm. Unlike individual cellulose nanofibers derived from plants that are not interconnected, the crosslinked gel structure of BC is expected to yield excellent intra-electrode conductivity after pyrolysis [34]. These nanoscale fibers also offer larger surface area compared to other cellulose materials composed of microscale large fibers [38–40]. It is interesting to note that some of the BC nanofibers exhibit a tubular-like or sheath structure (Fig. S2c and e), which seems not reported previously.

Pyrolysis of polymer and cellulose precursors, including BC, to derive carbon material has been commonly conducted in a thermal process with N_2 or Ar environment at temperature more than 800 °C for a few to more than 10 h [29,31]. Micropore activation during this long-duration thermal process, through physical decomposition and chemical etching is also a very common practice for achieving a large surface area for electrode applications. However, as will be demonstrated, this energy-consuming thermal pyrolysis process to introduce micropores, is detrimental for the electrode frequency response, and therefore is not suitable for HF-ECs.

The concept of employing RF or microwave plasma for manufacturing carbon fibers from natural or artificial sources was developed quite long ago with a vision of scaling down the power consumption, overall cost and volume of waste chemical products [41]. However, this technique has not been used in EC research area. In our study, BC aerogel was pyrolyzed in microwave plasma using a microwave plasma chemical vapor deposition system [42]. We have observed that a short period (15 min) plasma pyrolysis of BC produced electrodes with excellent electronic conductivity, large interconnected pores for rapid electrolyte ion migration, and reasonable surface area. Without employing any further treatment, such as structural modification, doping of electrode material or applying metallic current collector that were commonly used in other studies, the obtained CBC freestanding electrode was demonstrated to be very suitable for HF-ECs.

After plasma pyrolysis, the sample area was shrunk to about 30% and the mass was largely reduced. The morphology of CBC membrane is shown in Figs. 1f and S4. The overall structure is highly porous with meso- and macro-pores formed by the well-connected carbon nanofibers (CNF). The textural properties of CBC membrane were further characterized by N_2 sorption measurements (Fig. S5). A Brunauer–Emmett–Teller (BET) surface area of 57.5 m^2 g^{-1} is measured, with a pore volume of 0.374 cm^3 g^{-1}. The pore size distribution shows a minimum pore diameter of 3.8 nm and the CBC is dominated by meso- and macro-pores. Without micropores, slit pores, and dead end pores,