



Highly nitrogen-doped graphitic carbon fibers from sustainable plant protein for supercapacitor

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ABSTRACT

In this research, a novel biomass-based, highly nitrogen-doped carbon fiber material has been synthesized from electrospun plant protein fibers by one-step carbonization. The material fibrous structure was well maintained during pyrolysis by incorporating Ca²⁺ in the protein fiber matrix, since Ca²⁺ increased the thermal stability of the protein and the calcium salt/oxide provided a solid support during pyrolysis. In addition, the calcium salt served as a template to generate pores on the carbon samples. X-ray photoelectron spectra showed that the fibrous carbon materials possessed large nitrogen content (7.5%), mainly in the form of pyridonic/pyrrolic and pyridinic nitrogen. The optimized sample P-10% Ca-CL exhibited an interconnected carbon fiber network with meso and micropores on the fiber surface. Moreover, the well aligned granular graphitic structure observed embedded within the carbon fibers, which has been found for the first time from biomass derived carbon fiber materials. The optimized carbon fibers (P-10% Ca-CL) showed an exceptional areal specific capacitance of 64 μF/cm² at 0.5 A/g. This is attributed to the large number of N functional groups which induced a pseudocapacitance and improved the wettability of the carbon surface. The carbon fibers also exhibited excellent cyclic stability with 98% retention after 5000 cycles at a current density of 10 A/g. This research is the first publication of highly N-doped carbon fibers derived from plant proteins and show potential to be used as a supercapacitor electrode. Additionally, these materials were prepared by a convenient and environmentally-friendly method, not requiring a large energy input or corrosive chemicals.

1. Introduction

A supercapacitor is an electrochemical energy storage device with a large power density and rapid charge-discharge rate, thus has the potential to fill the technology gap between batteries and conventional capacitors (Pandolfo and Hollenkamp, 2006; Qian et al., 2014). Among supercapacitors, the electrochemical double layer capacitor (EDLC) stores energy by the reversible electrostatic accumulation of ions on the surface of porous electrodes (Béguin et al., 2014). Carbon is widely used as a supercapacitor material, due to its excellent cyclic stability, good electronic conductivity, low cost, and wide operating temperature range (Frackowiak, 2007). Carbon materials with various structures, such as carbon fibers, aerogels, tubes, sheets and particles, have been developed to accommodate to different application conditions (Frackowiak, 2007; Chen et al., 2012). Besides a well-tailored architecture, surface chemistry also plays an important role in determining the capacitance of carbon-based EDLCs (Wang et al., 2012). Introducing heteroatoms, such as nitrogen and oxygen, to the carbon matrix has

been proven effective to enhance the specific power density and energy density of EDLCs. Here, heteroatomic functional groups provide pseudocapacitance by Faradic redox reactions and/or chemisorptions. Moreover, such heteroatomic functional groups enhance the wettability of the carbon surface (Chen et al., 2012; Qian et al., 2014; Wang et al., 2012). Nitrogen – one of the most popularly studied heteroatoms – can be incorporated into carbon materials by *in situ* synthesis using N-rich carbon precursors and/or by treating carbonaceous materials with N-reagents (Hao et al., 2013).

Using sustainable biomass to synthesize materials for energy applications has attracted great attention as an alternative to fossil energy. For example, chitin derived from seafood waste has been turned into elastic nitrogen-doped carbon microspheres for applications in energy storage materials (Duan et al., 2016). Other raw materials, such as coconut shell, (Sun et al., 2013) corn stalks (Wang et al., 2013a) and resins (Li et al., 2013a), can also be converted to carbon materials. Despite the extensive studies and applications on converting carbohydrates and lipids into carbon and biofuels, proteins have not been

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utilized to synthesize energy storage materials. Proteins contain a large amount of N and O on their polypeptide chains, thus have the potential to be used as precursors for the preparation of heteroatom-doped carbon (Li et al., 2012; Qian et al., 2014). The N and O atoms from proteins may enhance the capacitance and improve the surface wettability, as well as the electronic conductivity of carbon materials (Hou et al., 2015). However, due to the thermal plastic nature of most proteins, the polypeptide chains would become flexible above glass-transition temperature and lose their structure during carbonization. Thus, one of the biggest challenges of using proteins as nitrogen-doped carbon precursors is to preserve their structure during carbonization when making the desired architecture, large surface area and large nitrogen content (Cho et al., 2015). One attempt was made to prepare hierarchically porous N-doped carbon from egg white protein using silica mesoporous cellular foam as a template. After carbonization at 850 °C, the egg protein-derived carbon contained 6% nitrogen and showed excellent Li⁺ storage capacity (Li et al., 2013b). However, the silica template preparation was both time and energy consuming. Moreover, the silica template had to be removed by hydrogen fluoride which is very corrosive and is a big concern for both human and environmental health. Thus, an effective method is needed to fabricate high-quality N-doped carbon from proteins.

In the leather manufacturing industry dating back to ancient times, metal ions were added to ‘fix’ the leather. This process involves a metal-collagen protein interaction that gives the product better mechanical strength and thermal stability (Deng et al., 2008; Liao and Shi, 2005). Inspired by this leather processing tradition, we added calcium salt to the protein matrix with the intention of maintaining the fibrous structure during carbonization. In this study, zein and hordein, two of the most abundant and affordable cereal proteins, were selected as the carbon precursors. Zein and hordein are the by-products of cereal processing and biofuel industries (Anderson and Lamsal, 2011; Wang and Chen, 2012a). They are relatively hydrophobic and can be dissolved in acetic acid solution. Our previous studies showed that their mixture could form electrospun fibers with good tensile strength without the addition of synthetic polymers – a feature conferring these proteins an advantage compared to most other plant proteins (Wang and Chen, 2012b). During electrospinning, hordein molecules have an extended and flexible conformation and interact with each other to form fibers (Wang and Chen, 2012a). We hypothesized that Ca²⁺ might modify the protein fiber bundles to retain the protein fibrous structure during thermal treatment; just as metal ions do in leather preparation.

The addition of Ca²⁺ may influence the conductivity and viscosity of the protein electrospinning dope and consequently modulate the diameter of the protein fibers (Kim et al., 2007; Zong et al., 2002). Thus, the morphology of Ca²⁺-protein electrospun fibers should be studied. Since calcium acetate may serve as a template to generate pores on carbon samples and can be easily washed away after carbonization, it was selected to facilitate the conversion of protein fibers into carbon fibers in this research. The influence of Ca²⁺ on protein fiber diameter and morphology was investigated. X-ray photoelectron spectroscopy (XPS) was used to study N and O functional groups on the carbon surface. The feasibility of using these carbon samples as supercapacitor electrode materials was evaluated and discussed.

2. Experimental section

2.1. Materials

Barley grains (Falcon) were kindly provided by Dr. James Helm of Alberta Agricultural and Rural Development, Lacombe, Alberta. Hordeins were extracted from barley grain using an ethanol solution according to a procedure reported in our previous work (Wang and Chen, 2012b). Zein (F4000, 92% protein content) was kindly provided by Freeman Industries LLC (New York, NY, USA) and used without further purification. Calcium hydroxide, polyvinylidene fluoride

(PVDF, molecular weight ~275,000 by gel permeation chromatography), N-methyl-2-pyrrolidone (NMP) and acetic acid were purchased from Sigma-Aldrich Canada Ltd (Oakville, ON, Canada). Glutaraldehyde solution (50%) and carbon black Super P was obtained from Fisher Scientific (ON, Canada) and Alfa Aesar (Ward Hill, MA, US), respectively. All chemicals were used as received unless otherwise specified. Ultrapure water, purified using a Milli-Q Advantage A10 system (EMD Millipore Corporation, MA, USA), was used to prepare electrolytes.

2.2. Preparation of plant protein-calcium electrospun fabrics

To prepare the protein-calcium acetate mixture for electrospinning, a desired amount (4–12%, w/v) of calcium hydroxide was slowly added to 2 mL acetic acid solution (90%, v/v) and stirred for 2 h to form calcium acetate. Plant protein solutions (18%, w/v) were then prepared by dissolving protein powders (hordein:zein = 50:50, w/w) in the acetic acid solution with calcium acetate, and stirred for 12 h at room temperature. The electrospinning experiments were carried out by a customized digital electrospinning apparatus EC-DIG (IME Technologies, Eindhoven, Netherlands) at room temperature. Solutions were forced through a blunt needle with a diameter of 0.8 mm at a flow rate of 1 mL/h. The spinning voltage was fixed at 20 kV and the needle to collector distance was 20 cm. The electrospun fabrics were collected on a rotary collector with a rotating speed of 1 rpm. The electrospun protein-calcium fibers were cross-linked by placing on a pan flowing above 200 mL of 25% (v/v) glutaraldehyde solution in a sealed glass container for 6 h at room temperature (Yang et al., 2008).

2.3. Carbonization

The carbon fibers were synthesized by one-step carbonization of the protein and calcium acetate electrospun fiber fabrics by heating in a tubular furnace (GSL-1100X-NT-UL, MTI Corporation, CA, US). In a typical experiment, the carbonization step was operated under continuous argon environment with the following heating procedure: (1) the temperature was raised from 25 to 200 °C at a speed of 5 °C/min; (2) the temperature was held at 200 °C for 2 h; (3) the temperature increased from 200 to 300 °C at a rate of 1 °C/min; (4) the temperature continued to increase from 300 to 850 °C at 5 °C/min; (5) the carbonization temperature was held for 2 h; (6) the sample was cooled down naturally under argon flow. Finally, the carbon sample was immersed in 2 mol/L hydrochloride solution to remove the calcium oxide and other soluble substrates, and then rinsed with water and dried at 100 °C under vacuum. The carbon samples derived from electrospun fabrics with varied amounts of calcium hydroxide were coded as P-4% Ca, P-8% Ca, P-10% Ca and P-12% Ca, respectively. The cross-linked sample was named with a suffix CL. For example, the carbon fiber sample derived from cross-linked electrospun fabric made with 10% Ca(OH)₂ was named P-10% Ca-CL.

2.4. Fiber size and morphology observation

The exterior morphology of the original fiber and the carbon fiber samples were observed by a Hitachi X-650 scanning electron microscope (SEM, Hitachi, Japan) at 20 kV. The original fiber samples were sputtered with gold before observation. High resolution transmission electron microscope (HRTEM, JEOL 2100, JEOL Inc., US) was used to study the microstructure of carbon fiber samples. For HRTEM observation, samples were ground into powders before deposition onto the 300 mesh Cu/Pd grids for observation. Fiber diameters were determined from SEM images with the ImageJ image-visualization software developed by the National Institute of Health (Wang and Chen, 2012b). Two hundred random positions were selected and measured for each sample.

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