High energy density supercapacitors from lignin derived submicron activated carbon fibers in aqueous electrolytes

Sixiao Hu [a], Sanliang Zhang [b], Ning Pan [b, **], You-Lo Hsieh [a, *]

[a] Fiber and Polymer Science, University of California-Davis, One Shields Avenue, Davis, CA 95616, United States
[b] Department of Biological and Agricultural Engineering, University of California-Davis, One Shields Avenue, Davis, CA 95616, United States

HIGHLIGHTS

- Super-fine highly porous activated carbon fibers (ACFs) were derived from lignin.
- Lignin-derived ACFs were fabricated into supercapacitor via vacuum filtration.
- ACFs achieved excellent 344F g^{-1} specific capacitance and 8.1 Wh kg^{-1} energy density.
- KOH ACFs exhibited exceptional total capacitance of 1 F at 10 mg loading.
- Lignin-derived ACFs exhibited over 96% capacitance stability after 5000 cycles.

GRAPHICAL ABSTRACT
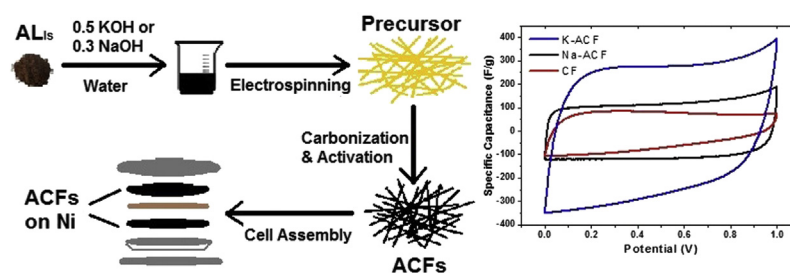
ABSTRACT

Highly porous submicron activated carbon fibers (ACFs) were robustly generated from low sulfonated alkali lignin and fabricated into supercapacitors for capacitive energy storage. The hydrophilic and high specific surface ACFs exhibited large-size nanographites and good electrical conductivity to demonstrate outstanding electrochemical performance. ACFs from KOH activation, in particular, showed very high 344 F g^{-1} specific capacitance at low 1.8 mg cm^{-2} mass loading and 10 mV s^{-1} scan rate in aqueous electrolytes. Even at relatively high scan rate of 50 mV s^{-1} and mass loading of 10 mg cm^{-2}, a decent specific capacitance of 196 F g^{-1} and a remarkable areal capacitance of 0.55 F cm^{-2} was obtained, leading to high energy density of 8.1 Wh kg^{-1} based on averaged electrodes mass. Furthermore, over 96% capacitance retention rates were achieved after 5000 charge/discharge cycles. Such excellent performance demonstrated great potential of lignin derived carbons for electrical energy storage.

1. Introduction

Activated carbon fibers (ACFs) are highly porous carbon in the fibrous form usually produced via activation of carbon fibers (CFs). The fibrous form of ACFs makes them easy to handle and to be further processed into various forms of sheets, felts and composites. The high specific surfaces, short diffusive paths and abundant accessible pores to sorbates are desirable characteristics of ACFs for removing toxic gases such as SO_2 [1], NO_x [2], organic compounds from air [3] and in waste water [4] as well as in storing hydrogen [5], methane and ethane [6]. Besides those excellent attributes, the high electrical conductivity of ACFs make them good candidate for supercapacitors, a pulse energy storage and delivery device used in the pitch system of wind turbines [7], electric vehicles [8] and

actuators [9] to physically uptake and release charges accumulated at the interface of carbon material and the electrolyte. To date, ACF based supercapacitors have been made from phenolic resin fibers in organic electrolytes [10,11] as well as polyacrylnitrile fabrics [12] and polyamic acid electrospun fibers [13] in aqueous electrolytes, yielding a specific capacitance from 113 to 208 F g^{-1}. However, these SCF precursors are energy consuming and expensive to produce and non-renewable. Moreover, the micro porous and carbon structures of those ACFs are not targeted for storing aqueous electrolyte ions. In fact, the electrolyte ions storage capacity of carbons critically depends on the amount of accessible surface area, and such accessibility is largely determined by the micro porous structure and composition, size, defects of the nanographite and the amorphous sp^2 carbon. Overall, high microporosity and wettability [14,15], larger nanographite size and less distorted bond angle [16] favor the adsorption of electrolyte ions. Therefore, it is desirable to fabricate ACFs with controlled micro porous and carbon structures for supercapacitor applications via simple and efficient processes from greener sources.

Lignin is the over 50 million metric tons per year worldwide chemical pulping and biofuel production by-product [17]. With only a small fraction being burned as low-valued fuel [18], lignin represents a significantly under-utilized biomass. The high carbon content and extensively crosslinked polypropanoid structure make lignin an excellent precursor for various carbon materials [19]. Activated carbon particulates have been produced by activation of kraft lignin using alkali hydroxide [20,21], zinc chloride and phosphoric acid [21]. Carbon fibers have been melt spun from softwood and hardwood kraft lignin aided by polyethylene oxide (PEO) [22] and polyethylene terephthalate [23], respectively, and coaxially electrospun from alcell lignin in ethanol [24]. Activated carbon fibers (ACFs) could also be melt spun from acetic acid softwood lignin then steam activation [25] or electrospun from Alcell lignin in ethanol then activated by oxygen-containing species [26]. Recently, we have also electrospun submicron fibers from aqueous alkali lignin with low sulfonate content (AL_{ls}) in-situ impregnated with alkali hydroxide and then simultaneously thermal processed and activated into ACFS in a single-step process [27]. The AL_{ls} based ACFs have very high specific surface (up to 1400 m^2 g^{-1}) with over 85% attributed to micropores at ca. 0.7 nm average pore size and remaining mesopores. Such abundant micropores are considered ideal for adsorption of aqueous KOH electrolytes and the mesopores are beneficial to electrolyte transfer to the micropore regions [15], both characteristics being highly promising for applications as supercapacitors.

In this work, AL_{ls} based ACFs were prepared from both NaOH and KOH activation (Na-ACF and K-ACF) and constructed into electrodes and supercapacitors. The electrical conductivities, wettability and microstructures of the ACF electrodes were first evaluated. The electrochemical properties of the ACF supercapacitor cells were thoroughly examined in terms of their specific capacitance from both cyclic voltammetry (CV) and galvanostatic charge/discharge curves, equivalent series resistance (ESR), energy and power densities, as well as cycling stability.

2. Experimental

2.1. Materials

Poly(ethylene oxide) (PEO) (Mw ~600 kDa) and alkali lignin with low sulfonate content (AL_{ls}, Mw ~ 60 kDa, spruce origin) were purchased from Sigma–Aldrich (USA), and sodium hydroxide (anhydrous pellets, A.C.S. grade, 85% minimum purity) and potassium hydroxide (anhydrous pellets, A.C.S. grade 97% minimum purity) were acquired from Fisher Scientific (USA). Nickel foam

(≥95% porosity with 80–100 PPI and 1.6 mm in thickness) and button cell case (CR2032) were purchased from MTI Corp (USA). All the materials were used as received.

2.2. Synthesis of activated lignin carbon fibers

Activated carbon fibers were prepared according to a previously reported method [27]. Briefly, aqueous 9/1 w/w AL_{ls}/PEO (10 wt% total concentration) mixtures and without or with alkaline hydroxides at 0.3 NaOH/lignin and 0.5 KOH/lignin were electrospun into CF, Na-ACF and K-ACF precursors, respectively. The electrospun precursor fiber mats were rolled and placed in a quartz tube (2 cm inner diameter) of an electric furnace (Mini-Mite, Lindberg/Blue). Carbonization (and simultaneous activation for ACFs) was performed by first heating to 105 °C to drive off the moisture, then heating to 850 °C, both at 10 °C min^{-1} heating rate and held at each temperature for 0.5 h under flowing N_2 at 100 mL min^{-1}. The heat processed fibers were cooled to ambient temperature within 12 h, under flowing N_2 at 100 mL min^{-1}. CFs and both ACFs were then washed with deionized water to remove residual alkali metals and other small hydrocarbon impurities, followed by oven drying at 105 °C for 0.5 h.

2.3. Construction of electrode and supercapacitor cell

The CF and ACF mats were dispersed in water (1 g L^{-1}) and sonicated (2510, Branson) for 30 min. The electrodes were prepared by vacuum filtration [28] of either CF or ACF suspensions to deposit onto nickel foams (shown in Scheme 1a). The weight of nickel foam per electrode is ca. 60 mg. The loaded mass of CF and Na-ACF was weighed to be 5.4 and 3.2 mg, respectively and the mass of K-ACFs varied from 1.8, 3.5, 7.5 to 10.0 mg and denoted as K-ACF-1, 2, 3 to 4. The resulting electrodes were roller pressed to 0.1–0.2 mm thickness and mold punched into 1.5 cm diameter circular shaped cells. The supercapacitor cells were constructed by using two identical electrodes with cellulose filter paper as separator into symmetric button cells (Scheme 1b) and sealed with a manual crimper (CR2032, MTI). 6 M aqueous KOH was the electrolytes.

2.4. Analytical methods

The chemical structures of CF and ACFs were examined by Fourier transform infrared spectroscopy (FTIR) (Nicolet 6700, Thermo Scientific). All FTIR spectra were collected using samples
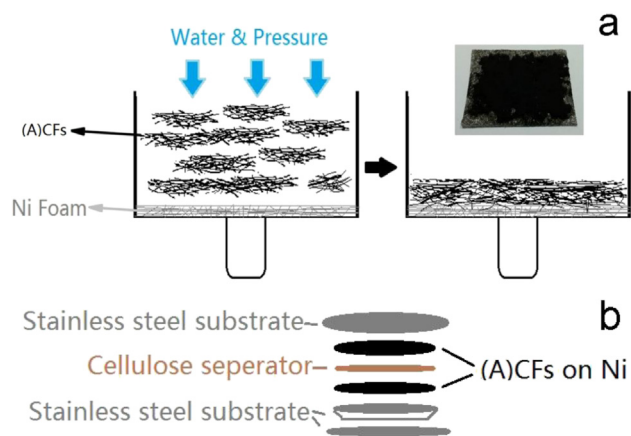
Scheme 1. Construction of (a) an electrode by CF and ACF deposition onto nickel foam via vacuum filtration (inset image: photo of an electrode); (b) a symmetric supercapacitor button cell.