Facile Preparation of Self-Standing Hierarchical Porous Nitrogen-Doped Carbon Fibers for Supercapacitors from Plant Protein–Lignin Electrospun Fibers

Jingqi Yang, Yixiang Wang, Jingli Luo, and Lingyun Chen

1Department of Agricultural, Food and Nutritional Science, University of Alberta, T6G 2P5 Edmonton, Canada
2Department of Food Science and Agricultural Chemistry, Macdonald Campus, McGill University, H9X 3V9 Montreal, Québec, Canada
3Department of Chemical and Materials Engineering, University of Alberta, T6G 2V4 Edmonton, Canada

ABSTRACT: This research aims to develop self-standing nitrogen-doped carbon fiber networks from plant protein–lignin electrospun fibrous mats for supercapacitors. The challenge in preparing carbon fiber from protein is to maintain a fibrous structure during carbonization process. Thus, lignin was incorporated with protein. At protein-to-lignin ratio of 50:50 to 20:80, the electrospun fibers maintained their structure after carbonization and formed self-standing carbon fiber mats. Stacked graphene layer structure was developed in the carbon fibers at a relatively low carbonization temperature (<1000 °C) without the use of catalysts, which might be derived from both lignin and protein. Graphene layer structure conferred the carbon fibers with superior conductivity. The optimized carbon fiber networks possessed excellent capacitance performance in 6 M KOH of 410 F/g at 1 A/g and good cyclic stability. Such good electrochemical properties were due to the well-engineered characteristics of the materials, including a hierarchical porous texture, heteroatoms (nitrogen and oxygen), and the stacked graphene layer structure. This research not only has provided a convenient way to develop carbon fibers from plant protein–lignin for N-doped supercapacitor electrodes, but also opportunity to add value to plant proteins and lignin as by-products of agricultural industry processing.

INTRODUCTION

Supercapacitors have attracted extensive attention in recent years because of their high power densities, rapid charging time, and long cyclic stability.1 They show promise to meet the increasing power demand for energy storage systems in various applications.2 Supercapacitors can be classified into two categories: electrical double-layer capacitors (EDLCs) and pseudocapacitors.3 EDLCs are based on the adsorption of electrolyte ions on the surface area of conductive materials, which are favorable in commercial utilization currently because of their superior cycle stability.

Carbon materials are widely used to produce EDLCs because of their good electrical conductivity and relatively low cost. The capacitance of EDLCs is related to the specific area of the electrodes. Activated carbon fibers have attracted interest because of their ability to build up hierarchical porous structures, namely, macropores in combination with meso- and micropores, with a large length/diameter ratio, surface area, and pore volume.4 They not only provide large surface area to store energy but also possess a shortened ion transport time.5 Currently, template casting, solvothermal synthesis, and chemical vapor deposition methods are applied to prepare carbon fiber precursors. However, these methods have limitations such as material restrictions, high cost, and process complexity.6 Electrospinning is a relatively convenient method to directly fabricate fiber networks, where the electrospun fiber composition, diameter, and alignment can be modulated to achieve a desirable structure and performance.7 Incorporating heteroatoms such as nitrogen and oxygen into the carbon framework is an effective strategy to improve the EDLC performance. N-doping has been shown to induce pseudocapacitance to carbon materials by additional faradaic redox reaction and/or chemisorption.8–10 N-rich biomaterials, such as protein and chitosan,11 are environmentally friendly precursors to prepare N-doped carbon materials.12,13 Proteins, rich in N and O, are one of the most abundant biomaterials on earth. Previous reports showed that the carbon samples derived from biomass rich in proteins, such as albumin,14 hair,1 silk cocoon,9 gelatin,15 and chicken eggshell membranes,16 possess high capacitance of more than 200 F/g. However, to the best of
our knowledge, protein-based carbon fibers with a hierarchical porous structure have not been reported as a supercapacitor material.

Zein and hordein are the major alcohol-soluble storage proteins (prolamins) in corn and barley, respectively. Zein is the byproduct of corn starch processing and the major coproduct of bioethanol production. Hordein is largely available as the byproduct of starch and β-glucan extraction. Development of value-added products from zein and hordein would benefit cereal growers and processors as well as reduce the wastes. Nanoﬁber fabrics based on the mixture of zein and hordein have been developed by our previous work via electrospinning. Such fabrics contain a large amount of N in the polypeptide chains and show good tensile strength, controllable diameter, and continuous ﬁber network. These are important attributes to create hierarchical porous nitrogen-doped carbon ﬁbers with superior capacitive performance.

The challenge in developing energy storage materials from electrospun zein/hordein protein nanoﬁber fabrics is to maintain a ﬁbrous mat structure because of the thermoplastic nature of proteins. To overcome this challenge, lignin is incorporated with plant protein. Lignin, one of the most important renewable resources on earth, contains abundant aromatic components, which allows it to be a good carbon precursor. Under proper heating conditions, lignin would aid in the development of a hierarchical porous structure.

However, lignin is challenging to be electrospun in many cases because of its susceptibility to “beading” resulting from the low molecular weight and low viscosity of lignin in solution. In this study, for the ﬁrst time, lignin will be incorporated with plant protein in acetic acid aqueous solution to prepare electrospun ﬁbers. The effects of protein–lignin ratio on carbon fiber morphology and electrochemical performance were evaluated. The potential and mechanism of proteins forming a graphitic structure were preliminarily investigated in this study. The electrochemical performance of the carbon ﬁber network was also tested.

## RESULTS AND DISCUSSION

**Morphology of Protein–Lignin Electrospun Fibers and the Derived Carbon Fiber Mats.** It was challenging to maintain the protein ﬁber networks during the carbonization process up to 900 °C because proteins are thermoplastic materials and often melt and lose their original structure at carbonization temperatures. The amorphous regions of protein molecules become mobile above the glass-transition temperatures (139 and 125 °C for zein and hordein, respectively). Crystalline regions then melt above the melting temperature before decomposition at even higher temperatures. To overcome this problem, lignin was added to sustain the ﬁber structure because it can transform from a thermoplastic to a thermosetting type during a continuous heating process. Continuous ﬁbers with smooth surfaces and uniform diameters were successfully prepared for the ﬁrst time from a plant protein–lignin mixture formula without the Figure 1. The lignin suspension alone showed poor electrospinning properties because lignin molecules have insufﬁcient chain structure, intermolecular interactions, and/or entanglements. Thus, the formation of continuous electrospun ﬁbers was attributed to the good electrospinnability of hordein and zein. Previous experiments by Wang and Chen showed that the hordein/zein mixture at a ratio of 1:1 exhibited a stable assembled network structure with good tensile strength. Thus, this hordein/zein ratio was used in the preparation of protein–lignin electrospun ﬁbers. Comparing protein–lignin ﬁbers with those from protein alone, the increase of lignin content from 0 to 50% increased the diameter of the ﬁbers from 0.54 ± 0.153 to 2.61 ± 7.2 μm. When the lignin ratio increased to 50%, the viscosity of the mixture increased (data not shown). The increased viscosity may be related to the interaction between lignin and proteins via hydrogen bonding. It was reported that increased viscosity contributed to the larger ﬁber diameter because higher cohesiveness of the electrospun dopes requires more force to elongate the ﬁbers. However, when the lignin content increased from 50 to 80%, the diameter of the ﬁbers decreased to 0.85 ± 0.24 μm. The addition of lignin to 80% signiﬁcantly affected the protein’s electrospinnability. The interruption of protein interactions resulted in a lower viscosity, leading to a smaller ﬁber diameter.

Carbon ﬁber samples with different protein–lignin ratios showed signiﬁcantly different morphologies (Figure 2A,C,E). A balanced protein–lignin ratio strongly inﬂuenced the compatibility of these two biopolymers to determine the structures of the carbon products. Samples of 100% protein melted during heating, and no ﬁber structure was formed (Figure S1). The ﬁbrous structure of L2P8 was partially lost after carbonization. The broken ﬁber network made L2P8-900 sample loss its self-standing property. L5P5-900 samples showed a continuous and smooth ﬁber structure after carbonization, and the ﬁber network was maintained. This was likely due to the good compatibility between protein and lignin at such a ratio, allowing both of them to be homogenously distributed within the ﬁber network. As shown in the inserted image of Figure 2C, the carbon ﬁber mat of L5P5-900 was self-standing and ﬂexible, having potential to be used in pliable supercapacitors with many applications, such as portable personal electronics. When the protein-to-lignin ratio decreased to 20:80 (L8P2), the electrospun ﬁbers also maintained their structure after carbonization and the carbon ﬁber mat was self-standing.
**Chemical Features.** Hordein and zein contain about 16% (w/w) nitrogen. Thus, the plant protein–lignin electrospun fiber is a nitrogen-rich carbon fiber precursor. In the LSPS fiber, the nitrogen and carbon contents were 7.0 and 56.7% (w/w), respectively. Carbon materials doped with heteroatoms, such as nitrogen, are expected to have an enhanced surface wettability, electronic conductivity, and capacitance. X-ray photoelectron spectroscopy (XPS) analysis was conducted to evaluate the chemical composition of the developed carbon fibers. As shown in Figure 3 and Table 1, nitrogen and oxygen were still maintained in the carbon networks after carbonization. Specifically, C 1s, O 1s, and N 1s were the three major peaks in the XPS spectra of L2P8-900, L5P5-900, and L8P2-900 (Figure 3A). The N content was increased as the protein ratio increased. For the LSPS-900 sample, 20.1% of the nitrogen in protein–lignin fibers was reserved even after the carbonization and activation processes.

The nitrogen functional groups were further investigated after deconvolution of the N 1s spectrum. As demonstrated in Table 1 and Figure S3, four overlapped peaks centered at 398.4, 399.9, 400.6, and 401.5 eV were observed and assigned to N-6 (pyridinic N), N-5 (pyrrolic N and/or pyridonic N), N-Q (quaternary N), and N-X (oxidized N), respectively. N-5 was the major N functional group of all three samples. L2P8-900, L5P5-900, and L8P2-900 contained 55, 37, and 49% N-5, respectively. N-6, N-5, and N-X were considered as the nitrogen groups located at the edge of graphene layers. N-Q represents nitrogen bonded to three carbon atoms and was more likely to be found in the central position of graphene sheets. Plentiful edge N groups were reported to be more active in contributing to the electrochemical performance. Pyridinic (N-6) and pyrrolic N (N-5) were assumed to be the main configurations introducing pseudocapacitance to the carbon materials, whereas N-Q was beneficial to the conductivities of carbon materials. The higher protein ratio resulted in higher amount of edge N groups. The edge N groups accounted for 80.4, 75.6, and 71.2% of total N.

**Figure 2.** Field emission SEM images of carbon samples: L2P8-900 (A,B), L5P5-900 (C,D), and L8P2-900 (E,F). (B,D,F) Enlarged view of carbon samples L2P8-900, L5P5-900, and L8P2-900, respectively. The scale bars in (A,C,E) were 10 μm. The scale bars in (B,D,F) were 100 nm. The photograph inserted in (C) demonstrates the flexibility of LSPS-900.

**Figure 3.** XPS spectra (A), HR-TEM images (L2P8-900 (B), LSPS-900 (C), and L8P2-900 (D) with a scale bar of 2 nm), XRD patterns (E), Raman spectra (F), and nitrogen adsorption and desorption isotherms (G) of L2P8-900, L5P5-900, and L8P2-900.
Table 1. Elemental Composition, Distribution of N Functional Groups Obtained by Fitting the N 1s XPS Spectra, and Pore Texture of Carbon Samples Derived from Plant Protein—Lignin Electrospun Fibers

| Sample     | C % | N % | O % | N-6 | N-5 | N-Q | N-X | S_{BET} (m^2/g) | S_{mac} (m^2/g) | APR (nm) |
|------------|-----|-----|-----|-----|-----|-----|-----|----------------|----------------|----------|
| L2P8-900   | 89.16 | 1.94 | 8.90 | 8.3 | 55.3 | 19.6 | 16.8 | 560.52          | 387.92         | 1.3      |
| L5P5-900   | 92.86 | 1.41 | 5.73 | 19.5 | 36.6 | 24.4 | 19.5 | 758.14          | 613.48         | 1.3      |
| L8P2-900   | 94.00 | 1.33 | 4.27 | 16.8 | 49.1 | 28.8 | 5.3  | 1113.16         | 683.16         | 1.4      |

aAtomic concentrations are presented in the table. The elemental composition was calculated based on the results of XPS spectra. bSurface area of micropores was calculated by using the t-pore method. cAPR represents average pore radius.

functional groups in L2P8-900, L5P5-900, and L8P2-900, respectively. This result revealed that the higher the protein—lignin ratio, the more the edge N groups in the final carbon sample. A protein consists of at least one linear long chain of amino acid residues linked by peptide bonds and folded into 3D conformation. After carbonization, hordein and zein are both high in proline residue (21% in hordein and 10% in zein), which has a pyrrolidine side chain, and glutamine residue, both high in proline residue (21% in hordein and 10% in zein), which has an amine group in the side chain. Other N atoms are in the form of the secondary amine groups in the peptide bonds. These results indicated that for higher plant protein—lignin ratio samples, amine groups were more likely to be converted into pyrrolic N, pyridinic N, and oxidized N located at the edge of the graphene layers during carbonization. L2P8-900, L5P5-900, and L8P2-900 were also high in oxygen, with 8.9, 5.7, and 4.3% oxygen, respectively. The spectra of C 1s (Figure S2) showed the existence of C–O, C–OH, and O==C–OH.

It was interesting that the carbon fiber was composed of a stacked graphitic layer structure, as demonstrated in the high-resolution transmission electron microscopy (HR-TEM) images (Figure 3B–D). The graphitic layers stacked and folded together with the layer-to-layer distance (d-spacing) among sheets being around 0.38 nm, similar to the spacing of the (002) distance of the graphitic carbon lattice (0.34 nm).27 Because of the intrinsic properties of graphene, these graphitic layers could improve the electrode performance by speeding up the transport of electrons and by increasing the in-plane conductivity.28 The graphitic structure was also confirmed by X-ray diffraction (XRD) and Raman spectroscopy.

XRD in the wide-angle region was used to evaluate the structure arrangement of the carbon samples (Figure 3E). The XRD patterns of three carbon samples derived from plant protein—lignin electrospun fibers were similar, having two peaks at around 23 and 44°. The wide and broad peak at 23° (002 lattice plane) indicated the existence of layer-by-layer graphitic stacking,28 further confirming the stacked graphitic layer structure observed by HR-TEM. The d_{002} (an interlayer spacing of 002 plane) can be calculated by the following equation: 

\[ d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \]

where \( \lambda \) is the wavelength of X-ray used. Thus, d_{002} of L5P5-900 was 0.387 nm, which was greater than but rather close to that of the pristine graphite of 0.34 nm.36 The increase of d-spacing was possibly caused by the presence of oxygen and nitrogen functional groups.36 The insertion of O and/or N caused changes in the reacting carbon atoms. The out of planar C–N or C–O covalent bonds resulted in the atomic scale roughness and thus increased the distance between graphene layers.40,41 Furthermore, the peak at 44° corresponded to the graphite (100) crystal plane.42

Raman spectroscopy was employed to reveal the quality of graphitic structure of carbon samples. As shown in Figure 3F, two major bands appeared in the 500–2500 cm⁻¹ region, including the D band at 1344 cm⁻¹ and the G band at 1595 cm⁻¹. The intensity of the D band is related to the vibration of C atoms with dangling bonds in planar terminations of defective and/or disordered graphite. The G band, on the other hand, is an indicator of the 2D graphite, corresponding to the vibration of sp² C in a 2D hexagonal lattice.33 Thus, the ratio of G/D band intensities (I_G/I_D) illustrates the crystalline degree of carbon materials. I_G/I_D values of L2P8-900, L5P5-900, and L8P2-900 were 1.00, 1.01, and 1.01, respectively, indicating the existence of graphite structure in carbon samples derived from protein–lignin electrospun fibers, albeit with disorder. The high protein ratio resulted in a slightly higher amount of defective structure. The I_G/I_D values of these carbon samples were less than those of the pristine natural graphite, which can be attributed to the introduction of oxygen and nitrogen functional groups into the carbon network.23,44 The relatively high graphitization degree may offer good electric conductivity, which was consistent with HR-TEM and XRD results.

Traditionally, the production of graphene materials has been challenging, including the high production cost and the demand for high energy input and the corrosive reagents, which limited their application as a commercial material for supercapacitors.35,46 This study demonstrated that a porous graphitic layer stacked structure can be created at a lower temperature (<1000 °C) without the use of a catalyst. The carbon precursor and the carbonization conditions both determine the structure of the final carbon material.2 The addition of lignin can transform the product from amorphous carbon to nanocrystalline graphite because it permits nucleation, growth, and clustering of aromatic rings during pyrolysis from 600 to 1000 °C.47 On the other hand, proteins may have the potential to form a stacked graphitic layer structure.35,48 As shown by thermogravimetric analysis (TGA) (Figure S3A), the decomposition of the protein electrospun fibers began at around 200 °C, above the glass-transition temperatures of hordein and zein. At this temperature, the Fourier transform infrared (FTIR) spectra (Figure S3B) showed that the protein denatured and its secondary structure dramatically changed. The amide I band (1700–1600 cm⁻¹) in the FTIR spectra is the prominent vibrational band of the protein backbone and is correlated with protein secondary structures.49 Protein electrospun fibers possessed one major peak at 1652 cm⁻¹, which was assigned to α-helix. After heating to 200 °C for 2 h, α-helix decreased, whereas β-sheets structure increased, as indicated by rising peaks at 1692, 1683, and 1623 cm⁻¹.50,51 The β-sheets are considered as crystal-dominant lamellar structures because they consist of polypeptide backbones connected and organized into pleated sheets by inter-/intramolecular hydrogen bonds. β-Sheets can transform into aligned hexagonal polycrystalline structure with pseudographitic crystalline lattice through cyclization or aromatization by intermolecular dehydration or condensation between adjacent polypeptide chains.48,52,53
Thus, it is possible that hordein and zein formed the stacked graphitic layers based on their β-sheet secondary structure during carbonization. However, the synergistic effects of protein and lignin need to be investigated further to better understand the formation mechanism of these graphitic layers.

**Porous Texture.** Methods to increase the specific surface area of carbon materials include chemical activation (using NaOH, KOH, ZnCl₂, phosphoric acid, etc.) and physical activation (heating under steam, air, carbon dioxide, etc.). Heating under CO₂ gas flow is an efficient treatment to increase the pore volume and surface area as well as to control the pore size distribution and surface chemistry of carbon materials by partial gasification of the carbon surface. As compared to chemical activation methods, no post-treatments are required after CO₂ activation, which makes it an environment-friendly activation method. To further improve the structure and properties of plant protein–lignin-based carbon fibers, they were pyrolyzed at 850 °C for 3 h under a CO₂ atmosphere.

Figure 2B,D,F demonstrates the pores on the fiber surface.

As shown in Figure 2C,E, the LSP5-900 and L8P2-900 samples maintained their continuous and interconnected fiber network after carbonization and activation. The interconnected large macropores formed by fiber interlacement could facilitate the ion transportation by serving as ion-buffering reservoirs and providing a low resistance for ion transportation from bulk electrolyte solution into carbon inner porous structures. This could subsequently contribute to the high rate capability and high power density of carbon materials. Under higher magnification (Figure 2D,F), the carbon fiber surface was porous and composed of a large number of meso- or micropores, likely formed during the CO₂ activation step. These numerous open pores can not only greatly increase the surface area but also improve the electrolyte ion accessibility by providing larger transport pores for diffusion from the surface to inner porous structures.

Figure 3G shows the nitrogen adsorption–desorption isotherms of carbon samples. As shown in Table 1, the total specific surface areas of L2P8-900, L5P5-900, and L8P2-900 were calculated to be 561, 758, and 1113 m²/g, respectively. The surface areas of LSP5-900 and L8P2-900 were higher than those of other carbon fibers reported in the literature. The specific surface area of electrospun nanofibers was strongly dependent on the diameter of fibers. The specific surface area of the nanofibrous membrane can be enhanced by reducing the diameter of fibers. As compared to LSP5-900 and L8P2-900, the relatively low surface area of L2P8-900 was due to the collapse of the fibrous structure after carbonization. The diameter of L8P2-900 fibers was smaller than that of LSP5-900, but their large open macropores could still contribute a high specific surface area.

Figure 4. (A) CV curves of L2P8-900, L5P5-900, and L8P2-900 at a scan rate of 25 mV/s; (B) CV curves of L8P2-900 at different scan rates from 10 to 50 mV/s; (C) galvanostatic charge–discharge curve of L8P2-900 at different current densities from 0.5 to 10 A/g; (D) gravimetric specific capacitance of L2P8-900, LSP5-900, and L8P2-900; (E) EIS Nyquist plots of L8P2-900 (inset shows the high- and medium-frequency regions) in a two-electrode system; and (F) cyclic stability of L8P2-900 at a current density of 5 A/g.
resulted in a higher surface area and external surface area. The average pore sizes of these three carbon samples were around 1.3–1.4 nm. The nitrogen adsorption and desorption isotherms of the three samples had a similar pattern. The adsorption behavior of nitrogen on carbon sample surface showed an initial large uptake in the low-pressure region ($P/P_0 < 0.1$), followed by a gradual increase in the mid $P/P_0$ region and then a slight increase in the high-pressure region ($P/P_0 > 0.9$). The carbon samples, especially L5P5-900 and L8P2-900, had high nitrogen adsorption at very low relative pressure ($P/P_0 < 0.1$), which was a typical indicator of the existence of a large amount of micropores. The isotherm continuously increased until a high $P/P_0$ value and did not saturate even at $P/P_0$ of about 1, which meant that this carbon material consisted of abundant mesopores and/or macropores. The hysteresis loop of nitrogen adsorption–desorption isotherm is associated with the capillary condensation of nitrogen in the pores; thus, the shape of the hysteresis loop is usually used to exhibit the specific porous structures. Because the adsorption and desorption branches were approximately parallel to each other over an appreciable range of $P/P_0$, the hysteresis loop could be classified as type H4, which was known to be related to the narrow slit-like pores. The hysteresis loop was observed from $P/P_0$ of about 0.1–0.95, which proved the coexistence of microporous, mesoporous, and macroporous structures in the carbon fiber mats.

**Electrochemical Performance.** The structure and chemical feature of carbon materials derived from protein–lignin electrospun fabrics triggered our interest to further investigate their electrochemical performance. Thus, cyclic voltammetry (CV), galvanostatic charge–discharge profile, and electrochemical impedance spectroscopy (EIS) were used to test the feasibility of carbon fibers as a supercapacitor electrode material using 6 M KOH as the electrolyte.

Figure 4A exhibits the CV curves of L2P8-900, L5P5-900, and L8P2-900 at a scan rate of 25 mV/s. The CV curves displayed a relatively good rectangular shape, indicating a typical characteristic of double-layer capacitance. As shown in Figure S4, the CV curve of L5P5-900 without activation exhibited a triangle shape, which demonstrated the existence of pronounced ion sieving effect. In such a case, the microrange pores were too small and excluded out the electrolyte ions during scanning. The CV curve of L5P5-900 was turned into rectangular after activation, demonstrating a good capacitive behaviour. This showed that CO2 activation opened up pores that were closed, clogged, or obstructed and created meso- and macropores at the surface of the carbon fibers. As shown in Table 1, the major pore radii of carbon samples were around 1.3–1.4 nm, which were larger than that generally required for the accommodation of aqueous electrolytes (0.4–0.8 nm). L2P8-900 had a smaller capacitance as compared to L5P5-900 and L8P2-900, which was caused by its smaller specific surface area. Moreover, L5P5-900 and L8P2-900 can be used for freestanding and binder-free electrodes. Figure 4B shows that the current density continuously increased as a function of scan rate for L8P2-900. The CV curve still maintained a quasi-rectangular shape even at scan rate as high as 50 mV/s, exhibiting excellent ion transport behavior and rapid charge propagation capability. This favorable characteristic was likely to be related to its hierarchic porous structure and partial graphitization. The interconnected porous structure provided a rapid ion transport pathway. The stacked graphic layer structure endowed the carbon fibers with high electron mobility because of its zero-gap semiconductor nature. The CV curves of L5P5-900 (Figure SSA) showed a similar quasi-rectangular shape even at scan rates as high as 100 mV/s.

The reversible capacitive behaviors of plant protein–lignin-based carbon fibrous samples were confirmed by the symmetrical triangle shape of the charge–discharge curve. The charge–discharge curves of L8P2-900 at different current densities via a three-electrode system are shown in Figure 4C. The charge–discharge curves of L5P5-900 are shown in Figure SSB. The specific capacitances of L8P2-900 and L5P5-900 were about 410 and 360 F/g at a current density of 1 A/g, respectively. Those are among the best gravity specific capacitance for carbon material supercapacitors. The areal specific capacitances of L8P2-900 and L5P5-900 were 36.85 and 47.48 μF/cm² at a current density of 1 A/g, respectively, which surpassed the area-normalized specific capacitances of active carbon (10–20 μF/cm²) and many carbon materials reported recently, such as N-doped hollow carbon nanofibers with an areal specific capacitance of 28.1 μF/cm² at 0.2 A/g and carbon nanofibers from lignin with 11 μF/cm² at 0.4 A/g. Though L2P8-900 had a relatively low gravity specific capacitance of 254 F/g, its areal specific capacitance was 45.31 μF/cm² at 1 A/g, which demonstrated the contribution of pseudocapacitance from N and O functional groups. The edge N groups were reported to provide significant pseudocapacitance to the carbon surface. L5P5-900 and L8P2-900 had more than 200 F/g even at a high current density of 10 A/g. The freestanding ability and high specific capacitance of L5P5-900 and L8P2-900 allowed them to be favorable for large-scale applications, such as highly compact electric power source.

EIS is a powerful technique for characterizing the properties of electrode–electrolyte interfaces of supercapacitors and provides information about the internal resistance of the electrode materials and the resistance between electrode and electrolyte. The Nyquist plots of L8P2-900 are shown in Figure 4E. In the low-frequency region, a straight vertical line was obtained, indicating a near-ideal capacitive behavior of the L8P2-900 carbon sample. The projected length of the Warburg-type line (the slope of the 45° portion of the Nyquist plots) on the Z’ axis was widely accepted to demonstrate the characterization of ion diffusion process in the electrode. The knee frequency of L8P2-900 was 40 Hz. The onset frequency, defined as the highest frequency where the impedance of electrode begins to be dominated by the capacitive behavior, was 25 Hz for L8P2-900. The Warburg-type line of L8P2-900 was rather short, directly proving that the carbon material had a short electrolyte diffusion pathway because of its hierarchical porous structure, which is important for a low ion transport resistance and high rate capability and power density. A resistance of 2.76 Ω obtained by extrapolating the vertical portion of the plot to the real axis confirmed a low equivalent series resistance value of the L8P2-900 electrode system.

As exhibited in Figure 4F, 95% of the initial capacitance of L8P2-900 was maintained after over 3000 charge and discharge cycles at a current density of 5 A/g. The long-term stability of L5P5-900 is shown in Figure SSD. This result indicated that L8P2-900 and L5P5-900 carbon materials had excellent long-term charge–discharge cyclic stability, which would make them feasible for use in many industrial and personal applications.
CONCLUSIONS

This is the first time that a convenient method has been developed to prepare nitrogen-doped and self-standing carbon fibers from plant proteins and lignin with a high energy storage capacity. Carbon fiber mat L8P2-900 possessed a specific capacitance of 410 F/g and 35.8 μF/cm² in 6 M KOH and 95% capacitance retention after 3000 charge–discharge cycles. These excellent electrochemical properties were due to the well-engineered characteristics of the materials, including a hierarchical porous texture, an interconnected fiber network, a large amount of heteroatoms (nitrogen and oxygen), and the stacked graphene layer structure. Carbon fibers derived from plant protein–lignin electrospun fibers have the potential to be used as new and effective energy storage devices. Environmentally sustainable industrial applications could be developed from this technology, such as portable electronic devices, hybrid electric vehicles, and the management of large-scale power systems.

MATERIALS AND METHODS

Materials. Barley grains (Falcon) were provided by Dr. James Helm, Alberta Agriculture and Rural Development, Lacombe, AB, Canada. Hordeins were extracted from barley grains using an ethanol solution according to a previous work.35 Zein (F4000, 92% protein content) was provided by Freeman Industries LLC (New York, NY, USA) and used without further purification. Alkali lignin, polyvinylidene fluoride (PVDF, molecular weight ~275 000 by gel permeation chromatography), N-methyl-2-pyrrolidone (NMP), potassium hydroxide, and acetic acid were purchased from Sigma-Aldrich Canada Ltd (Oakville, ON, Canada). Dimethylformamide (DMF) and carbon black super P were obtained from Fisher Scientific (Ottawa, ON, Canada) and Alfa Aesar (Ward Hill, MA, US), respectively. All chemicals were used as received unless otherwise specified.

Preparation of Plant Protein–Lignin Electrospun Fibers. Lignin and plant protein (hordein/zein = 50/50, w/w) powders were dissolved in a mixed solution of acetic acid and DMF (90/10, v/v) and stirred for 12 h. The total content of polymers was 36% (w/v). The lignin and protein blending ratios were 20/80, 50/50, and 80/20 (w/w). Correspondingly, their electrospun fiber samples were coded as L2P8, L5P5 and L8P2, respectively. The electrospinning experiments were carried out on a customized digital electrosprinning apparatus EC-DIG (IME Technologies, Eindhoven, Netherlands) at 25 °C. 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 fiber fabrics were collected on a collector with a rotating speed of 1 rpm.

Carbonization and Activation. The carbon fibers were synthesized by carbonizing the protein and lignin electrospun fiber mat in a tubular furnace (GSL-1100X-NT-UL, MTI Corporation, Richmond, CA, US), followed by a carbon dioxide activation step. In a typical experiment, protein–lignin nanofiber mats underwent the following heating procedure under continuous purge of air to stabilize their structure: (1) temperature raised from 25 to 250 °C at a rate of 1 °C/min; (2) from 250 to 900 °C at 5 °C/min; (3) carbonization temperature held for 2 h; and (4) sample cooled down naturally under protection gas flow. Then, carbon fibers were activated at 850 °C under CO₂ gas flow (argon/CO₂ = 95:5) for 3 h to generate a porous structure on the carbon fiber surface. The sample cooled down naturally under CO₂ gas flow.

Fiber Size and Morphology Observation. The size and morphology of samples before and after carbonization were observed by a Hitachi X-650 scanning electron microscope (Hitachi, Tokyo, Japan) at 20 kV. The protein–lignin fiber samples were sputtered with gold for 2 min before observation. The surface pores of the activated carbon fiber were observed by a scanning electron microscope equipped with a cold field emission gun at 15 kV (S-4800 FE-SEM, Hitachi, Tokyo, Japan). Fiber diameters were determined from scanning electron microscopy (SEM) images with the ImageJ image-visualization software developed by the National Institute of Health.16 Two hundred random positions were selected and measured for each sample. A high-resolution transmission electron microscope (JEOL 2100, JEOL Inc., Peabody, MA, US) was further employed to study the microstructure of carbon fiber samples. For this, samples were ground into powders and then deposited onto the 300 mesh Cu/Pd grids.

Fiber Textural Characterization and Chemical Analysis. Autosorb iQ (Quantochrome Instruments, Boynton Beach, FL, US) was employed to measure the nitrogen adsorption–desorption isotherm, specific surface area, and porous texture at 77 K. The specific surface area and pore size distribution were calculated based on the Brunauer–Emmett–Teller (BET) theory and nonlocal density functional theory, respectively. The micropore and external pore surface area were calculated by the t-plot method. These analyses were done by the Autosorb iQ’s associated software (ASiQWin). Powder XRD patterns were obtained to show the crystallinity of carbon by using a Bruker AXS D8 DISCOVER diffractometer (Bruker Corporation, East Milton, ON, Canada) with the Cu Ka radiation (λ = 1.541841 Å) at 40 kV and 44 mA (20 was from 10 to 80°). Raman spectra were obtained to examine the carbon sample structure by a Nicolet Omega XR Raman microscope (Thermo Fisher Scientific, Waltham, MA, US). The excitation near-infrared laser wavelength was set at 532 nm, and data points were recorded at a 0.5 cm⁻¹ interval. The nitrogen and carbon contents of the protein–lignin fibers were measured by a Leco nitrogen analyzer (FP-628, Leco, St. Joseph, MI, US). XPS was applied to analyze the chemical composition of the carbon surface using an Axis Ultra spectrometer (Kratos Analytical, Manchester, UK). X-rays Al Kα (hv = 1486.6 eV) was used. The C 1s and N 1s core levels were fitted using the CasaXPS software to reveal the C and N configuration.

Electrochemical Performance Analysis. L2P8-900 samples were ground and mixed with 10 w/w % carbon black and 10% PVDF binder (10 w/w % in NMP) to form a paste. The paste was cast onto a piece of nickel foam in an area of 1.0 cm², dried under vacuum at 120 °C for 12 h, and then pressed under 2000 psi by a benchtop laboratory press (model 3851, Carver Inc., Wabash, IN, US) to fabricate an electrode. Because L5P5-900 and L8P2-900 samples were flexible and self-standing, they were used without binding treatment. To assemble a three-electrode cell, the above prepared nickel foam or fiber mats of L5P5-900/L8P2-900, a Pt wire, and a Hg/HgO electrode were used as working, counter, and reference electrodes, respectively.
All electrochemical properties were analyzed by an Autolab PGSTAT128N (Metrohm Autolab, Massauga, ON, Canada). CV studies were performed in the potential window of −1.0 to 0 V versus reference electrode at various scan rates from 5 to 50 mV/s. Galvanostatic charge–discharge curves were measured with a current density from 0.5 to 20 A/g. The specific capacitance of carbon materials was calculated by the following equation:

$$C = \frac{I \Delta t}{m \Delta V}$$

where \( I \) (A) is the discharge current, \( \Delta t \) stands for the discharging time, \( m \) (g) is the weight of the carbon sample loaded on the working electrode, and \( \Delta V \) represents the potential window. EIS was performed in a frequency range from \( 10^{-2} \) to \( 10^{6} \) Hz with 5 mV amplitude with a symmetrical two-electrode setup. To assemble symmetrical two-electrode cells, two pieces of nickel foil were used as current collectors. Carbon fiber mat was pressed onto nickel foam. Two pieces of identical carbon fiber mat were placed together and separated by a filter paper as a separator.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01876.

SEM images of carbon from protein fibers, deconvoluted XPS spectra of C 1s, TGA curve and deconvoluted FTIR spectra of protein fibers, CV curve of LSPS, and electrochemical properties of LSPS-900 (PDF).

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: lingyun.chen@ualberta.ca.* Phone: +1-780-492-0038.

ORCID

Jingqi Yang: 0000-0002-5762-5031
Yixiang Wang: 0000-0001-8386-7491
Jingli Luo: 0000-0002-2465-7280
Lingyun Chen: 0000-0002-8956-7358

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