# **Protein Powder Derived Porous Carbon Materials as Supercapacitor Electrodes**

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Protein-based microporous carbon (PMC) with high nitrogen, sulfur content and the specific surface area was obtained from commercial protein powder (PP) by KOH activation. Many interconnected micropores and mesopores were formed in the carbonization process, the specific surface area of the PMC was up to 1117 m<sup>2</sup> g<sup>-1</sup>. The nitrogen content is 15.29 at.%, sulfur percent is 0.71 at.% in the asprepared PMC. Both high specific area and heteroatom content bring the ideal capacitance characteristics when PMC was fabricated as supercapacitor electrodes. The different carbonization temperature and activation ratio of PP to KOH have been discussed to get the best electrochemical performances. The specific capacitance of PMC600-1:2 was up to 336 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>, much higher than that of commercial electrodes. The capacitance retention is 173 F g<sup>-1</sup> at 10 A g<sup>-1</sup>, indicating that the PMC owns good rate capability. At the same time, the cycling stability of the sample is 83 % after 10000 cycles at 10 A g<sup>-1</sup>. Furthermore, an as-fabricated PMC-based symmetric supercapacitor device shows a high energy density of 27 W h kg<sup>-1</sup> at a power density of 900 W kg<sup>-1</sup>.

Keywords: Microporous carbon, Nitrogen doping, Electrochemical performance, Supercapacitors

# **1. INTRODUCTION**

With the rapid development of modern society, more urgent demands as electrochemical capacitors or ultra-capacitors have attracted much attention because of their high power density, good reversibility, and long cycle life [1-3]. Due to their stable physicochemical properties, high electronic conductivity, optimized pore structure, high specific surface area and low cost, porous carbon materials

were considered as promising electrode materials for supercapacitors. [2-6]. The surface area of some porous carbon materials can reach 3000 m<sup>2</sup> g<sup>-1</sup>, but only about 10~20% of the "theoretical" capacitance was developed due to some micropores are not involved in the transmission of electrons [7, 8].

Recently, some researchers consider that the capacitance performance of carbon materials could be greatly improved through doping with heteroatoms (such as N, S, P, and B) in porous carbon system [9-11]. For example, Chen reported nitrogen-doped carbon materials from urea formaldehyde (UF) resin. The specific capacitance of the obtained carbon material reached 239 F g<sup>-1</sup> at the current density of 0.5 A g<sup>-1</sup>[12]. These heteroatoms not only increase the wettability of the carbon material, but also contribute pseudo-capacitance [12-14]. However, these synthesized polymers have more or fewer disadvantages such as intricate production, pollution and high production cost [15, 16]. Therefore, natural and renewable materials were introduced to supercapacitors [17-19]. Recently, silk, chitosan, grain, and gelatin had been applied as raw materials for preparing heteroatom-doped activated carbon due to their wide availability and good sustainability [20-26]. Up to date, few works on porous carbon materials derived from protein applied for supercapacitors were reported. Xu utilized the broad beans for the synthesis of sulfur/nitrogen dual-doped carbon materials [27]. Eggs are rich in protein. Thus, egg white, egg yolk, or egg membrane were exploited as precursors for preparing heteroatom-doped activated carbon with excellent capacitive performances [28-30].

Commercial protein powder includes two different kinds of protein, soy protein and whey protein, which are composed of various amino acids. In this work, commercial protein powder was used as the starting material to achieve microporous carbon with KOH as activator. The as-prepared PMC was further explored as supercapacitor electrodes and its electrochemical properties were investigated systematically.

## 2. EXPERIMENTAL

#### 2.1 Chemicals

0.4 g protein powder (PP) was pre-carbonized at 200 °C for 3h with the heating rate of 2 °C min in Ar atmosphere. PP and KOH were mixed in beaker (the mass of KOH was 0 g, 0.4 g, 0.8 g, 1.2 g, respectively). Then the activation was performed under a Ar flow at 600°C for 3 h. The obtained materials were washed with 1 mol/L HCl and deionized water successively until a neutral pH. Finally, the protein-based microporous carbon (PMC) was dried at 40 °C for 12 h. The electrode materials were noted as PMC600, PMC600-X (X represented the mass ratio of PP and KOH, which were 1:1, 1:2, 1:3, respectively). The PMC were carbonized at 500 °C and 700 °C with same conditions were called as PMC500-1:3, PMC600-1:3 and PMC700-1:3.

# 2.2 Characterization

The scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscope (TEM, Tecnai G2 F20) were employed to analyze the morphology of the samples at an accelerated

voltage of 20 KV and 200 KV, respectively. Thermal gravimetric analysis (TGA) measurements were performed on Perkin-Elmer, TG7, under N<sub>2</sub> flow (20 mL min<sup>-1</sup>) and the scanning rate was 10 °C min<sup>-1</sup> from 45 °C to 800 °C. The X-ray diffraction (XRD) patterns with a scan rate of 1° min<sup>-1</sup> of the samples were measured by a D8-ADVANCE X-ray diffractometer (Cu K $\alpha$  source,  $\lambda = 0.15406$  Å). Raman spectra were tested on a Laser Confocal Micro-Raman Spectroscopy (LabRAM HR800) with an excitation wave length of 532 nm and the argon ion laser source ranges from 600 cm<sup>-1</sup> to 3600 cm<sup>-1</sup>. The X-ray photoelectron spectroscopy (XPS) was obtained from Multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI) with the Al-Ka as the monochromatic source. The samples were estimated under the binding energy ranges from 0 eV to 1350 eV. The N<sub>2</sub> adsorption and desorption measurements were executed on a Geminiv2380 surface area and pore size distribution analyzer. The measurements of galvanostatic charge-discharge (GCD), cyclic voltammetry (CV), and electrical impedance spectroscopy (EIS) techniques were texted on a CHI660E electrochemical workstation in 6 mol L<sup>-1</sup> KOH aqueous electrolyte with the voltage range of -1.2~-0.2 V. And the frequency range for the EIS was from 10<sup>-2</sup> to 10<sup>5</sup> Hz with the open circuit potential. The specific capacitance ( $C_{sp}$ ) of electrode materials is calculated by equation (1)[9]:

 $C_{\rm sp} = (I \times \Delta t) / (m \times \Delta V) \tag{1}$ 

Where I represents the current (A),  $\Delta t$  represents the discharge time in GCD curve (s), m represents the mass of active material (g), and  $\Delta V$  represents the voltage window (V).

#### **3. RESULTS AND DISCUSSION**

# 3.1 Morphology and structure

The SEM images of PMC600 and PMC600-1:2 are shown in Fig. 1a, 1b and 1c, 1d, respectively. Fig. 1a shows the PMC600 looks like an uneven lump with diameter from a few to 50 microns. The surface of PMC600 is smooth and compact and no obvious micropores or mesopores are visible as shown in Fig. 1b. Fig. 1c exhibits the morphology of the PMC600-1:2 after KOH activation. The large lumps decomposed into small loose sphere-like aggregates and the size of the spheres is uniform compared that of PMC600. The more interesting is that the surface of the activated material becomes rough, as shown in Fig. 1d. More details can be observed from the TEM images Fig. 1e and 1f. A large number of pores with different diameters can be observed in Fig. 1e and the surface of the sample is coarse due to the existence of plenty of pores. Fig. 1f demonstrates more details about the pores on the surface of carbon materials that the diameter of the pores is between 1~50 nm which belong to micropores and mesopores.



**Figure 1.** SEM images of PMC600 (a, b) and PMC600-1:2 (c, d) at different magnifications; Low (e) and high (f) magnification TEM images of PMC600-1:2.

TGA which usually used to evaluate the thermal stability of the materials was performed, and the curve was shown in Fig. 2a. The initial weight loss below 120 °C reflects the loss of moisture of the samples. The large weight loss of PP at the temperature range from 220 °C to 400 °C is mainly due to the oxygen-containing functional groups removed. When the temperature exceeds 400 °C, the weight loss becomes slow because PMC were eventually converted into their carbonaceous analogues [31].

To further detect the chemical states and confirm the effects of nitrogen and sulfur in the carbon materials, XPS was performed, and the result was demonstrated in Fig. 2b. The characteristic binding energies are at about 166.34 eV (S2p), 286.24 eV (C1s), 400.72 eV (N1s) and 533.5 eV (O1s) in the XPS survey scans. Fig. 2c is the spectra for the C1s indicating the different species such as C=C, C-C, C=N, and C=O which were corresponded to binding energies at 284.4 eV, 285.0 eV, 285.5 eV and 287.8 eV, respectively [32, 33]. Fig. 2d is the N1s peak which can be convoluted into three peaks with the binding energy of 400.25 eV, 399.2 eV and 398.5 eV, demonstrating the existence of pyrrolic N, amino and pyridinic N [34-36]. As reported previously, pyridinic-N and pyrrolic-N can increase the specific capacitance of electrode materials by providing pseudo-capacitance [37, 38]. Two peaks centered at 530.9 eV and 532.7 eV appear in the narrow spectrum of O1s, which are related to the oxygen atoms of C=O and C-O in Fig. 2e [39]. Besides, the N and O atoms doped into carbon may enhance the wettability of electrode interface, and produce affluent faradic pseudo-capacitance in aqueous electrolytes [40, 41]. Four peaks centered at 164.3 eV, 165.2 eV, 168.5 eV, and 169.8 eV indicate the bonds of C-S-S-C-, C=S and sulfur oxides in Fig. 2f [1, 42]. The C, N, O and S content of PMC600-1:2 analyzed from XPS data are 71.79, 15.29, 12.21 and 0.71%, respectively, as shown in Table 1.

Table 1. Carbon, nitrogen, oxygen and sulfur contents (at. %) in PMC600-1:2.

Sample	С	Ν	0	S
PMC600-1:2	71.79	15.29	12.21	0.71



Figure 2. (a) TGA curves of the PP, XPS survey (b), C1s(c), N1s(d), O1s(e), S2p (f) of PMC600-1:2.

The S<sub>BET</sub> and detailed pore parameters for the as-prepared PMC had been listed in Table 2. The N<sub>2</sub> adsorption-desorption isotherms and pore size distribution curves of PMC600-1:1, PMC600-1:2 and PMC600-1:3 were shown in Fig. 3. It could be seen that the three samples exhibit an isotherm combined type I and IV isotherms. There is a narrow knee at a very low relative pressure ( $P/P_0 < 0.03$ ), indicating the existence of well-developed micropores [27]. PMC600-1:1, PMC600-1:2 and PMC600-1:3 shows an average pore size of 2.2, 2.0 and 1.7 nm respectively, as indicated in Table 2. The SBET and porosity of the resultant carbon materials were significantly influenced by the activation ratio of KOH to PP. With the ratio of KOH to PP increasing from 1:1 to 1:3, the S<sub>BET</sub> increases with the increasing amount of the KOH which hints more micropore and mesopore formed. However, the pore volume reaches it maximum 0.57 cm<sup>3</sup> g<sup>-1</sup> when the ratio of KOH to PP is 1:2. And the micropore and mesopore volume are 830 cm<sup>3</sup> g<sup>-1</sup> and 287 cm<sup>3</sup> g<sup>-1</sup>, respectively, and pore volume PMC600-1:3 has the largest specific surface area and the smallest average pore size which illustrates that the diameter of the pores becomes smaller and the number of the pores becomes larger. However, it is not certain that PMC600-1:3 will exhibit the best electrochemical performance as the electrode because some micropores are not involved in the transmission of electrons [26, 43-45]. So the electrochemical performances of PMC600-1:3 are not as good as that of PMC600-1:2 as described below.

Table 2. S<sub>BET</sub> and pore properties of the samples.

Sample	$S_{BET}$	$\mathbf{S}_{\mathrm{micro}}$	S <sub>meso/macro</sub>	$V_{pore}$	Dave
	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	(nm)
PMC600-1:1	709	482	227	0.40	2.2
PMC600-1:2	1117	830	287	0.57	2.0
PMC600-1:3	1217	988	227	0.53	1.7

The Raman spectra could reflect different graphite nature and defects during the carbonization and activation procedure of the samples. The Raman spectra of the PMC500-1:2, PMC600-1:2 and

PMC700-1:2 are conducted to determine the structural change of the porous carbon materials as shown in Fig. 3c. The peaks located at 1340 cm<sup>-1</sup> and 1586.8 cm<sup>-1</sup> can be indexed as D band and G band, arising from the disordered carbon structure and the vibration mode of the movement in opposite directions of two carbon atoms in a single graphene sheet. And the intensity ratio between D to G bands ( $I_D/I_G$ ) could exactly reflect the graphitic degree of the carbon materials. The ratio values are the 0.91, 0.94 and 0.95 respectively, hinting more breakdown of symmetry for small graphitic crystallites carbon atoms at the edge of grapheme layers although the extent of graphitization increases with the temperature increasing [46, 47]. The 2D centered about 2680 cm<sup>-1</sup> is the second order of the D band and caused by the double resonant Raman scattering with two-phonon emissions. Interestingly, the 2D is sensitive to the number of graphene layers, so the occurring of the 2D indicates the existence of multilayer graphene-like structure and increase of the graphitization [48]. This result is in good agreement with the analysis of the XRD.

Fig.3d shows the XRD patterns of PMC500-1:2, PMC600-1:2 and PMC700-1:2. One broad diffraction peaks were centered at around 23.1°, 24.2°, and 27.0° of 2 thetas signed the (002) plane of the hexagonal graphic carbon [16]. With the increasing of carbonization temperature, the (002) peaks of porous carbon materials shifts to a higher angle toward the right direction and the intensity of the peak is relatively weak, which suggests an increased degree of graphitization and a decreased crystallinity [49].



**Figure 3.** (a) N<sub>2</sub> adsorption-desorption isotherms, pore-size distributions (b), Raman spectra (c), XRD patterns (d), of the PMC600-1:1, PMC600-1:2 and PMC600-1:3.

#### 3.2 Electrochemical performances

Considering the multiple advantages of the PMC, such as high nitrogen content, high BET surface area, it should be a good candidate for supercapacitor electrodes with improved electrochemical performance. Its electrochemical properties were evaluated by CV, GCD and EIS technique as shown in Fig. 4. Fig 4a exhibits the CV curves of the four electrodes carbonized at a different temperature. The shapes of all CV curves show slightly deviation from rectangle, indicating the capacitive response comes from the combination of EDLC and pseudo-capacitance [50]. PMC600-1:2 has two redox peaks come from nitrogen and sulfur, like XPS results. Pseudo-capacitors are related to the doping of the heteroatoms which bring fast and reversible oxidation-reduction reactions reflected by reversible redox peaks. In this work, owing to the incorporation of nitrogen and sulfur heteroatoms within the PMC, those redox peaks were strong and obvious and the contribution of the pseudo-capacitance for the electrochemical performances of PMC600-1:2 became well-pronounced correspondingly. It is clearly that the surrounded area by CV curves of the three PMC electrodes is much larger than that of PC600, demonstrating the KOH activation plays an important role to improve its electrochemical characteristics. And the surrounded area of PMC600-1:2 is the largest among all the samples, indicating the best supercapacitor performances. As shown in Fig 4b and c, the Csp of the PMC600-1:2 is 336 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup> and its rate capability is the best (173 F g<sup>-1</sup> at 10 A g<sup>-1</sup>), implying that 600 °C is the optimal carbonization temperature among all the samples.



**Figure 4.** (Electro chemical capacitive behaviors of the porous carbons at the activation temperature from 500 °C to 700 °C CV at a scan rate of 10 mV s<sup>-1</sup> (a), GCD curves at current density of 1 A g<sup>-1</sup> (b), The dependence of capacitance as a function of current density (c), The Nyquist plots (d).

Fig. 4d shows the Nyquist plots of different PMC electrodes. Estimated from the diagram, the charge-transfer resistance of PMC600-1:2 is 0.5  $\Omega$ , much smaller than 3.8 and 1.2  $\Omega$ , corresponding to PMC500-1:2 and PMC700-1:2, indicating that the PMC600-1:2 has minimum resistance among the three electrodes which is beneficial to enhance its electrochemical performances as supercapacitor.

To further investigate the influence of activating ratio on the electrochemical performances, Fig. 5 shows the comparison of PMC600-1:1, PMC600-1:2, PMC600-1:3, PMC600 by CV, GCD, and EIS. The Fig. 5a exhibits that PMC600-1:2 has the largest surrounded area among the four electrodes. Fig. 5b shows the galvanostatic charge/discharge curves at a current density of 1 A  $g^{-1}$ . The specific capacitances are calculated from the discharge curves with values of 274, 336, 272 and 60 F  $g^{-1}$  for PMC600-1:1, PMC600-1:2, PMC600-1:3, PMC600, respectively. Interestingly, the highest capacitance was achieved for PMC600-1:2, which has only mediate BET surface area of 1117 m<sup>2</sup>  $g^{-1}$  but highest mesopore content of 25%. This result proves that different activation ratios of electrode materials to KOH bring difference in specific surface area and pore size, which further influence the ions adsorption and exchange [44].

In Fig. 5c, the specific capacitance of the PMC600-1:2 at different current densities is overtly higher than that of the PMC600-1:1 and PMC600-1:3. This should be ascribed to well-developed porosity of PMC600-1:2, which can decrease the ion diffusion resistance during charge-discharge process. The EIS tests could confirm this conclusion as shown in Fig. 5d, where PMC600-1:2 exhibits a straight line at low frequencies and small semicircular shape at high frequencies hinting fast charge diffusion to form EDLC. All the above results hint a fact that the PMC600-1:2 is the most appropriate ratio of PP to KOH.



Figure 5. Electrochemical capacitive behaviors of the porous carbons at the different powder/KOH ratios (1:1, 1:2, 1:3) CV at a scan rate of 10 mV s<sup>-1</sup> (a), GCD curves at current density of 1 A g<sup>-1</sup> (b), the dependence of capacitance as a function of different current densities (c), The Nyquist plots (d).

Fig. 6a shows the CVs of the PMC600-1:2 electrodes at scan rates of 10~100 mV s<sup>-1</sup>. There is no obvious shape distortion in the CV curves at the different sweep rate which suggesting a highly reversible system can be employed in KOH electrolyte within the potential range. The pseudocapacitance and double-layer capacitance lead to the high capacitance of PMC600-1:2. The GCD curves show nearly symmetric triangular shapes at different current densities (Fig. 6b), the resemble charge and discharge capacity prove good reversibility of materials. As depicted in Fig. 6c, the capacitance retention of PMC600-1:2 is 83% after 10000 charge-discharge cycles at the current density of 10 A g<sup>-1</sup> and a charge-discharge curve is intercepted in Fig. 6c inset. This result suggests that PMC600-1:2 displays excellent cycling stability.

In order to further obtain the power density and energy density of the material, the two-electrode test was texted in the 6 M KOH electrolyte, which can be calculated with Eqs. (2) and (3) as the following [51, 52]

$$E = CV^2/2$$
 (2)  
 $P = E/t$  (3)

Where *E* refers to the energy density (Wh kg<sup>-1</sup>), *C* is the specific capacitance of the total symmetrical system (F g<sup>-1</sup>) which is tested by two-electrode system, *V* represents the voltage drop during discharge (V), *P* represents the power density (W kg<sup>-1</sup>), *t* represents the discharge time (h).

The Ragone plot (Fig. 6d) shows that specific power density is about 900 W h kg<sup>-1</sup> (27 W Kg<sup>-1</sup>) at 0.5 A g<sup>-1</sup>, whereas it remains as high as 18000 W h kg<sup>-1</sup> (9W Kg<sup>-1</sup>) at 10 A g<sup>-1</sup>. In general, the energy densities of PC based SC devices based on an aqueous electrolyte are 3-5 W h kg<sup>-1</sup> and the power densities are less than 10 k W kg<sup>-1</sup>[27, 53].



Figure 6. Electrochemical characterization of the PMC-600-1:2 in 6 molL<sup>-1</sup> KOH aqueous electrolyte
GCD curves with different current densities (a). The CV curves at various scan rates (b). Cyclic stability at a current density of 10 A g<sup>-1</sup> over 10000 cycles (c). The ragone plot PMC600-1:2 (d).

Electrode materials	Activating agent	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Electrolyte	Current density	Specific capacitance (F g <sup>-1</sup> )	Ref.
PMC600-1:2	KOH	1117	6 M KOH	1 A g <sup>-1</sup>	336	This work
Yogurt	KOH	1300	6 M KOH	2 A g <sup>-1</sup>	225	[54]
Seaweeds	N/A	746	1 M H <sub>2</sub> SO <sub>4</sub>	0.2 A g <sup>-1</sup>	264	[55]
Silk	KOH	2557.3	1 M H <sub>2</sub> SO <sub>4</sub>	0.1 A g <sup>-1</sup>	264	[17]
Eggshell membrane	Air	221.2	1 M KOH	0.2 A g <sup>-1</sup>	297	[56]
Human hair	KOH	1306	6 M KOH	1 A g <sup>-1</sup>	340	[57]
Bamboo byproduct	KOH	1472	6 M KOH	0.1 A g <sup>-1</sup>	301	[58]

Table 3 Specific capacitance of reported carbon-based supercapacitors

Comparing the data reported in the literatures (Table 3), it is obvious that PMC600-1:2 exhibit better electrochemical performance than other biomass based carbon materials. That proves PMC600-1:2 is a promising candidate for electrode material as high performance supercapacitors.

## 4. CONCLUSIONS

In summary, PMC600-1:2 had been prepared with PP as precursor after carbonization at 600 °C and activation with KOH. The N content is high in the PMC which provides pesudo-capacitance. The specific surface area of the PMC600-1:2 is 1117 m<sup>2</sup> g<sup>-1</sup> due to many hole formed in the activation carbonized materials which are beneficial for electrolyte transport. The specific capacitance of PMC600-1:2 is 336 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>, 173 F g<sup>-1</sup> at 10 A g<sup>-1</sup> which indicates good rate capability. At the same time, the cycling retention is 83% after 10000 cycles in KOH electrolyte at 10 A g<sup>-1</sup>. This facile method provides a promising porous electrode doped with heteroatoms which may be applied in the field of supercapacitors.

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