

Article

Porous Doped Carbons from Anthracite for High-Performance Supercapacitors

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Abstract: Carbon-based materials, as some of the most important electrode materials for supercapacitors (SC), have spurred enormous attentions. Now, it is highly desirable but remains an open challenge to design stable and high-capacity carbons for further enhancing supercapacitive function. Here, a facile chemical activation recipe is introduced to develop biomass-derived functional carbons using cheap and abundant natural resources, anthracite, as the heteroatom-rich carbon sources, and potassium hydroxide (KOH) as activator. These porous carbons have high BET surface areas of roughly 2814 m² g^{−1}, large pore volumes of up to 1.531 cm³ g^{−1}, and a high porosity that combines micro- and small-sized mesopores. The optimal nanocarbon features two additional outstanding virtues: an appropriate N-doping level (2.77%) and a uniform pore size distribution in the narrow range of 1–4 nm. Synergy of the above unique structural traits and desirable chemical composition endows resultant samples with the much boosted supercapacitive property with remarkable specific capacitance at varied current densities (e.g., 325 F g^{−1} at 0.5 A/g), impressive energy/power density, and long cycling stability over 5000 cycles at 10 A g^{−1} (92% capacity retention). When constructing the symmetric supercapacitor utilizing a common neutral Na₂SO₄ electrolyte that can strongly circumvent the corrosion effect occurring in the strong acid/alkaline solutions, both an elevated operation voltage at 1.8 V and a fascinating energy density of 23.5 Wh kg^{−1} are attained. The current study paves the way to explore the stable, efficient, and high-voltage SC assembled by the anthracite-derived porous doped nanocarbons for a wide spectrum of applications like automobiles, vehicle devices, and so on.

Keywords: porous carbon; anthracite; supercapacitor; high energy density; nitrogen; biomass

1. Introduction

During past decades, both the aggravating resource depletion and exacerbating environmental pollution have stimulated tremendous efforts regarding pursuing the renewable/eco-friendly energy storage devices to gratify the insatiable demand [1,2]. As a result, supercapacitors as a kind of new and promising energy storage system have cut an increasing dash due to their fast charge/discharge rate, high power density, and long cycling stability [3,4]. Supercapacitors can be categorized into the electrochemical double-layer capacitors (EDLCs) and pseudocapacitors based on the energy storage mechanisms [5]. EDLCs store energy by means of reversible ion

adsorption in the double layer formed on the surface of inert electrodes, while pseudocapacitors deliver energy depending upon reversible redox reactions on active material's surface [6]. In the last few years, multifarious materials, including carbon-based materials, metal oxides/hydroxides, conducting polymers, and hybrid composites, have been extensively excogitated as supercapacitor electrode materials [7]. Among them, carbon materials, especially the porous carbons, are acclaimed as the most promising candidates as electrode materials for EDLCs, taking into account their high merits of the large specific surface area (SSA), well-designed pore size distribution (PSD), low cost, favorable chemical/thermal stabilities, precursor availability, environmental friendliness, and relatively high conductivity [8]. Nevertheless, pragmatic applications of porous carbon electrodes are still stifled because of the fatal disadvantage of low energy density ($3\text{--}5\text{ Wh kg}^{-1}$) [9]. It is well-known that the performances of supercapacitors are strongly swayed by SSA, PSD, electrical conductivity, and surface functionalities [10,11]. The SSA and PSD can universally constitute two pivotal factors dictating the capacitive performance of EDLCs [12]. In addition, the existence of heteroatoms (such as B, N, O, P, and S) can enhance specific capacitance by improving the wettability and inducing the pseudocapacitance [13]. For example, nitrogen doping has been deemed as the most feasible protocol to step up the surface wettability, electronic conductivity, and capacitive property of EDLCs [14]. Unfortunately, a high level of nitrogen doping inevitably renders the materials susceptible to the grim capacity deterioration during the long-term cyclic test as a result of the vulnerable material stability and the functionality decomposition. So far, it still remains a grand challenge to facilely develop the optimal porous doped carbon materials from inexpensive carbon sources. Therefore, to further tweak the electrochemical signature of EDLCs, the porous carbon electrode materials should be judiciously formulated with the particular intention of maximizing SSA, controlling the PSD, and modulating the doping heteroatom.

To fulfill the high-performance supercapacitors, it is thus imperative to develop an expeditious and straightforward scenario to synthesize porous carbons from the naturally rich and economically competitive carbon sources. Over years, a myriad of carbon resources, e.g., fossil-based hydrocarbons, agricultural and biomass by-products, and polymers, have been capitalized upon for the preparation of porous carbons [15]. Out of them, coals are cheap and abundant as the most commonly used materials. According to the literature, the porous carbon materials can be obtained utilizing different strategies: (i) physical activation with different oxidizing gases (e.g., H_2O or CO_2) [16]; (ii) chemical activation with chemical activating agents (e.g., KOH , NaOH , H_3PO_4 , or ZnCl_2) [17]; (iii) the templating avenue with templates (e.g., MgO , ZnO or organic molecules) [18]. In comparison with the physical activation, chemical activation needs a lower temperature and shorter time, and, more importantly, results in a more uniform PSD and higher SSA. Among various chemical activators, potassium hydroxide (KOH) is one of the efficient activation agents for fabricating porous carbons with fine-tuned textural properties [19]. More interestingly, activation by KOH can introduce a high amount of the oxygen/nitrogen-containing functional groups, thereby fostering the electronic conductivity and imparting the additional pseudocapacitances [12].

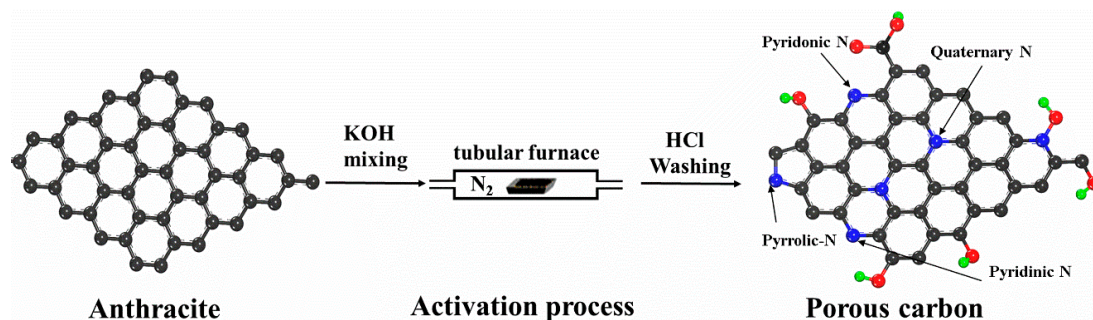
In this article, the porous carbon samples were successfully derived from anthracite through the chemical activation method with a KOH activator and then assessed for the supercapacitor application. Impressively, the optimized material featured the high SSA ($2814\text{ m}^2\text{ g}^{-1}$), uniform PSD ($1\text{--}4\text{ nm}$), and proper nitrogen content ($2.77\text{ at}\%$). Consequently, the as-resultant porous carbons manifested remarkable electrochemical performance, such as a superior specific capacitance of 325 F g^{-1} at the current density of 0.5 A g^{-1} , excellent cycling stability (92% of capacitance retention after 5000 cycles) at a large current density of 10 A g^{-1} in a 6 M KOH solution. More significantly, the as-fabricated symmetric supercapacitor device delivers a high energy density of 23.5 Wh kg^{-1} with a power density of 450 W kg^{-1} at the current density of 0.5 A g^{-1} in $1\text{ M Na}_2\text{SO}_4$ aqueous solution, transcending the most hitherto reported carbon materials. These exceptional performances of the porous carbon electrode can be attributed to its well-defined structural hallmarks of the high SSA, uniform PSD, and proper

nitrogen content. Our current study ushers in a compelling initiative to turn up the functional carbon materials for the energy storage fields.

2. Materials and Methods

2.1. Materials Synthesis

All the reagents used in the experiment were of analytical grade without further purification. The anthracite (Yunnan Province, China) was singled out as the carbon precursor. The proximate analysis and element analysis data of anthracite were shown in Table S1. The chemical activation of anthracite was performed using KOH as activating agent. The synthesis process of porous carbon is depicted in Scheme 1. In a typical synthesis, 3 g dried anthracite and 12 g KOH were physically mixed by high-speed multi-function milling. Subsequently, the resultant mixture was transferred to a nickel crucible and activated at 700–900 °C for 1 h in a horizontal tubular furnace with a heating rate of 5 °C min^{−1}. After that, the samples were cooled down to room temperature. The whole process was processed in an N₂ flow (50 mL min^{−1}). Finally, the products were filtered and washed with 5 M HCl solution and distilled water several times to remove the residual ions. Once the residual alkali was completely removed, porous carbons were dried at 100 °C for 24 h in an oven. The final product is designated as KAC-x, wherein x denotes the activation temperature (700, 800, and 900 °C). To effectively eliminate the heteroatom groups in KAC-800, the KAC-800 sample was thermally treated under N₂ at 900 °C for another 2 h and the as-obtained product was dubbed as KAC-800-900.



Scheme 1. Schematic diagram for the synthesis of porous carbon from anthracite.

2.2. Materials Characterization

The samples were characterized by X-ray diffraction (XRD) analysis using a DX-2700 instrument with a Cu K α radiation ($\lambda = 0.15418$ nm). The SSA and pore structure of the carbon samples were determined at 77 K using a NOVA1000e surface area and pore size analyzer (Quantachrome Company, Boynton Beach, FL, USA). The SSA was calculated by the conventional Brunauer–Emmett–Teller (BET) method, and the PSD was estimated from the adsorption branch isotherm by density functional theory (DFT) method. The structure was examined using Raman scattering spectra. Thermo-gravimetric analysis was executed harnessing a thermo-gravimetric analyzer (TGA Q500) in air flow (50 mL/min). The surface chemical composition of the samples was detected by X-ray photoelectron spectroscopy (XPS).

2.3. Electrochemical Analysis

The electrochemical measurements were carried out at room temperature in both three-electrode and two-electrode configurations. In the three-electrode system, all the electrochemical measurements were conducted on the CHI660e electrochemical workstation in 6 M KOH aqueous solution with Pt wire as counter electrodes and a Hg/HgO electrode as reference electrodes. The working electrodes were prepared by mixing the porous carbons, acetylene black, and polyvinylidene fluoride binder together in a weight ratio of 8:1:1 in *N*-methyl-2-pyrrolidone. The mixture was then pasted onto on the

1 cm × 1 cm nickel foam and dried at 100 °C overnight. The electrochemical cyclic voltammetry (CV) curves were recorded between a potential range of −1 and 0 V at various sweep rates. Galvanostatic charge–discharge cycling (GCD) tests were implemented at different current densities from 0.5 to 20 A g^{−1}. Electrochemical impedance spectroscopy (EIS) was monitored in the frequency range of 10 mHz to 100 kHz with an amplitude of 5 mV. The cycling stability test was evaluated by GCD measurements at a current density of 10 A g^{−1} for 5000 cycles. The specific capacitance was computed according to Equation (1):

$$C = \frac{I\Delta t}{m\Delta V} \quad (1)$$

wherein C (F g^{−1}) represents the specific capacitance, I (A) is the discharge current, Δt (s) is the discharge time, m (g) stands for the mass of active material in a single electrode, and ΔV refers to the voltage change during the discharge process.

In the two-electrode symmetrical supercapacitor cells, the electrodes were prepared by applying the previous method. The symmetric supercapacitors were built utilizing two equal electrodes equipped with a separator and nickel foam current collector and appraised in 6 M KOH (voltage range of 0–1 V) and 1 M Na₂SO₄ (voltage range of 0–1.8 V). Cyclic voltammetry (CV) was assessed at various scan rates. Galvanostatic charge/discharge curves were obtained at diversifying current densities to estimate the specific capacitance. The specific capacitance of the two-electrode symmetrical supercapacitor cell was gauged using the following Equation (2):

$$C_{cell} = \frac{I\Delta t}{M\Delta V} \quad (2)$$

where C_{cell} (F g^{−1}) means the total cell specific capacitance, I (A) deals with the current density, ΔV appertains to the potential change (V) within the discharge time Δt (s), and M concerns the total mass (g) of active materials in both electrodes.

The energy density and power density were calculated by using the following Equations (3) and (4):

$$E = \frac{1}{2}C_{cell}(\Delta V)^2 \times \frac{1}{3.6} \quad (3)$$

$$P = \frac{E}{\Delta t} \times 3600 \quad (4)$$

where E (Wh kg^{−1}) is representative of specific energy density; P (W kg^{−1}) signifies the specific power density of the symmetrical supercapacitor setup; ΔV (V) means the operation voltage for charging and discharging; and Δt (s) stands for the discharge time.

3. Results and Discussion

3.1. Effect of Thermal Treatment upon Supercapacitor Performance

In order to investigate the impact of thermal treatment upon the textural properties of the porous carbons, the N₂ adsorption/desorption isotherm profiles are measured. As seen from Figure 1, the isotherms are typical of type I, demonstrating that the porosity mainly originates from micropores, which is beneficial for ion storage during the charge/discharge process [20]. In the whole pressure region, the largest nitrogen adsorption volume of KAC-800 verifies its highest SSA. Detailed information on the textural properties of all samples is compiled in Table 1. The KAC-800 sample shows a high SSA of 2814 m² g^{−1} with a pore volume of 1.531 cm³ g^{−1}, which is higher than KAC-700 and KAC-900. The specific surface area contributed by the micropore filling is 1568 m² g^{−1} for KAC-700, 1935 m² g^{−1} for KAC-800, and 1658 m² g^{−1} for KAC-900. The corresponding PSD is delineated in Figure S1. It can be seen that the PSD curves of samples mainly reveal the existence of micropores and small mesopores with a size of 1–4 nm. The average pore size (d_M) is made larger with the increase in the activation temperature. As has been evidenced, the coexistence of micro/meso-scale pores is critically vital for

attaining the rapid ion transportation and high-power characteristics of supercapacitors [21,22]. It is obvious that structural signatures of porous carbons heavily hinge upon the activation temperature. The textural evolution here unveils that the activation temperature can function as an effective rudder to fine-tune the material structure and thus exert the striking ramifications upon the supercapacitor performance of the porous carbon electrodes.

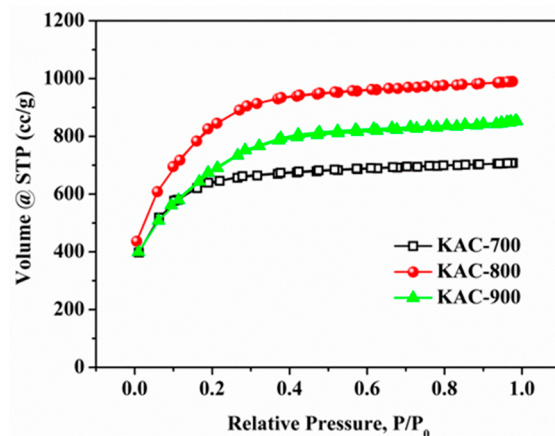


Figure 1. N_2 adsorption-desorption isotherms of samples.

Table 1. Textural properties of samples (calculated total surface area S_{BET} , total pore volume V_T , and average pore diameter d_M).

Samples	S_{BET} ($m^2 g^{-1}$)	V_T ($cm^3 g^{-1}$)	d_M (nm)
KAC-700	2041	1.095	2.145
KAC-800	2814	1.531	2.177
KAC-900	2337	1.319	2.223

Supercapacitive performances of the samples firstly came under evaluation in a three-electrode system by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) in 6 M KOH (Figure 2). The CV curves of all samples (Figure 2a) present rectangular-like shapes with signally broadened redox peaks, illuminating that the overall capacitance originates from a good combination of double-layer capacitance and pseudocapacitance contributed from nitrogen functional groups [16]. Moreover, the largest CV area of the KAC-800 may be associated with the greatest SSA of the sample activated at 800 °C, which can provide plenty of the electron/ion-active interfaces [23]. The exact specific capacitances quantified from GCD tests are displayed in Figure 2b. Notably, the KAC-800 electrode always delivers the highest capacitance at different current densities spanning between 0.5 and 20 $A g^{-1}$, with the specific capacitances of 325 and 216 $F g^{-1}$ being accomplished at 0.5 and 20 $A g^{-1}$, respectively. Moreover, it is clear that the specific capacitances for all samples encounter a gradual decrease with the rise in the current density because of the remarkable gain in the diffusion limitation inside pore channels [24].

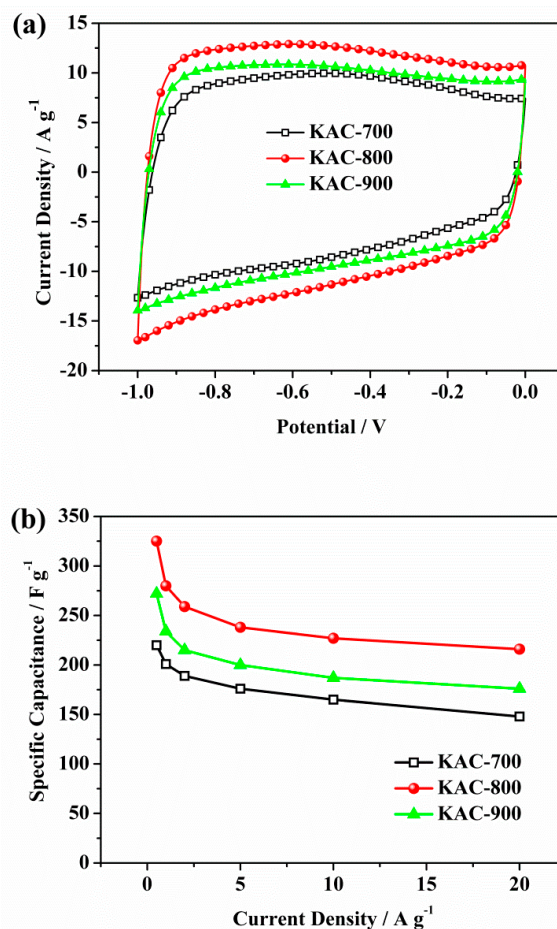


Figure 2. (a) CV curves of the porous carbons at the scan rate of 50 mV s^{-1} ; (b) specific capacitances of porous carbons as a function of the current densities.

Figure 3a portrays the CV profiles of KAC-800 under varying scan rates. The typical box-like shape is well maintained even at a very high scan rate of 200 mV s^{-1} , symptomatic of small equivalent series resistance, remarkable rate performance, and superior charge propagation [25]. All GCD curves of KAC-800 in Figure 3b illustrate the symmetrical attributes, mirroring the extraordinary capacitive properties [26]. In addition, the distinct distortion of GCD lines demonstrates the presence of nitrogen functional groups that could offer some pseudocapacitance, which coincides with the CV result [27].

The long-term cyclic lifetime is another critical figure of the merit for laying bare the practical feasibility of supercapacitors, in particular if the pseudo-capacitance comes into being. Therefore, the cyclic stability of the KAC-800 electrode was further examined at a large current density of 10 A g^{-1} . As seen in Figure 4, the specific capacitance retention of KAC-800 is as high as 92% even over the continuous 5000 GCD cycles, unravelling exceptional electrochemical sustainability [28]. Additionally, the 5000th GCD curve (inset in Figure 4) is still distinguished by a symmetrical triangular shape, unearthing that the electrochemical events on the electrode possess outstanding reversibility [29].

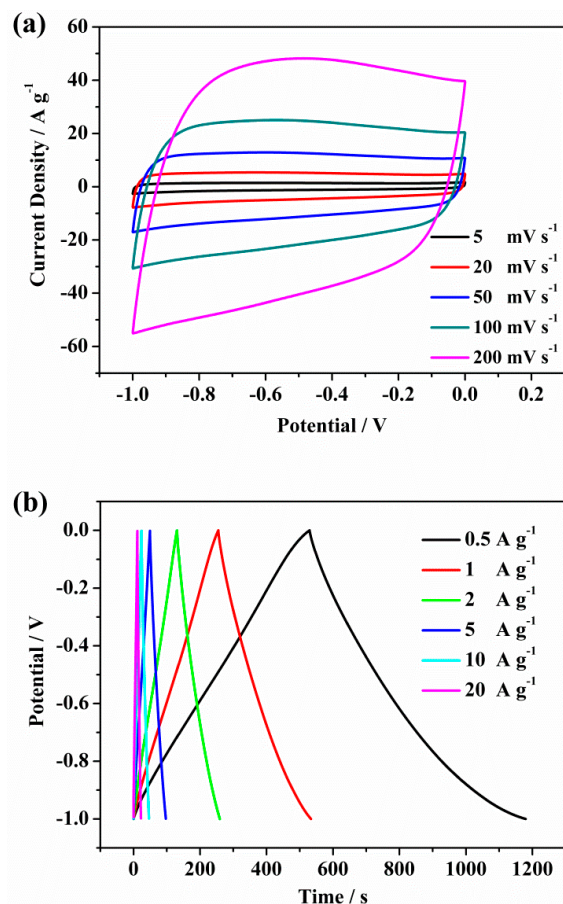


Figure 3. (a) CV curves of KAC-800 at different scan rates; (b) galvanostatic charge–discharge cycling (GCD) curves of KAC-800 at various current densities.

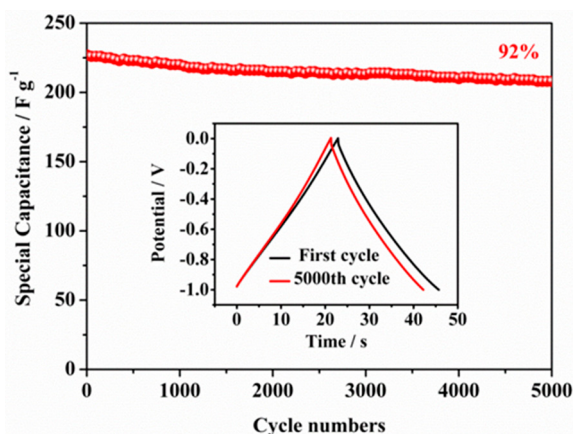


Figure 4. Cycling stability of KAC-800 at the current density of 10 A g⁻¹ for 5000 cycles. The inset shows the GCD lines of the first and 5000th cycles.

The phase structures of porous carbons are investigated by the XRD tools. As given in Figure 5, XRD patterns of all samples exhibit two broad and weak diffraction peaks centered at a 2θ degree of approximately 21° and 44° , which can be assigned to the (002) diffraction of the graphitic layer-by-layer structure and the (100) diffraction of graphite, respectively. This doubtlessly sheds light on the formation of amorphous carbon frameworks [30]. The low-angle region gains considerable intensity, clarifying the presence of a high density of pores [31]. This phenomenon also bolsters the observations from the N₂ volumetry.

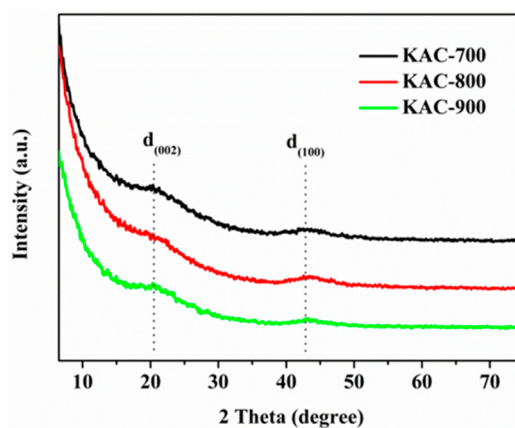


Figure 5. XRD patterns of samples.

3.2. Effect of Nitrogen Content on Supercapacitor Performance

To eliminate the nitrogen elements in KAC-800, the KAC-800 sample was subjected to a thermal annealing in N_2 at 900 °C for another 2 h. The textural properties of as-obtained KAC-800-900 were identified by N_2 adsorption-desorption measurement. The type I adsorption isotherm of KAC-800-900 (Figure S2) reflects its micropore-predominant structure, which is reminiscent of all above-mentioned samples. The corresponding PSD of KAC-800-900 (Figure S3) also falls into a narrow size range of 1–4 nm. Details regarding physical characteristics of KAC-800-900 are summarized in Table S2. It is noted that there emerges no obvious difference of SSA and PSD between KAC-800 and KAC-800-900. Plus, the XRD pattern of the KAC-800-900 (Figure S4) likewise resembles the counterpart of KAC-800. These results unambiguously expound that the further high-temperature treatment at 900 °C under N_2 for 2 h is non-destructive for textural properties of KAC-800. Nevertheless, taking into account the fact that their electrochemical properties are divergent, the reason behind this disparity must correlate with the influence from the other factor.

In the three-electrode test, KAC-800-900 shows a more rectangular curve with smaller area than KAC-800 (Figure 6a), uncovering its lower capacitance (Figure 6b) which can primarily emanate from the absence of the N-containing functional groups [32]. This conclusion can be confirmed by analysis of the elemental compositions and chemical states of the samples from XPS study. As shown in XPS survey spectra (Figure 7a), only the N signals are only spotted in KAC-800, revealing the existence of nitrogen-containing functional groups in KAC-800. As generalized in Table S3, the nitrogen contents are calculated to be approximately 2.77 at% and 0.08 at% for KAC-800 and KAC-800-900, explicitly highlighting that the high-temperature treatment can diminish the nitrogen species in KAC-800 to an extremely limited level which can impose the negligible impingement upon the pseudocapacitance contribution. C1s core-shell emission spectrum of KAC-800 (Figure 7b) can be compartmentalized into four envelopes, corresponding to C-C (284.6 eV), C=N/C-O (285.7 eV), C-N/C=O (286.7 eV), and O-C=O (289.8 eV) functional groups. Furthermore, the XPS N1s spectrum of KAC-800 (Figure 7c) could be deconvoluted into three kinds of nitrogen functional groups, including pyridinic (N-6, 398.1 eV), pyrrolic/pyridonic (N-5, 399.6 eV), and quaternary nitrogen (N-Q, 401.5 eV), validating that the nitrogen atoms inserted into KAC-800 are in different binding states [33]. Moreover, three types of the oxygen species are discerned for KAC-800 (Figure 7d). The peaks at roughly 531.1, 532.9 and 536.2 eV can appertain to C=O, C-O, and O-C=O groups, respectively [34]. These surface N-/O-containing groups will substantially ameliorate wettability and capacitive properties of porous carbon electrode materials for supercapacitors.

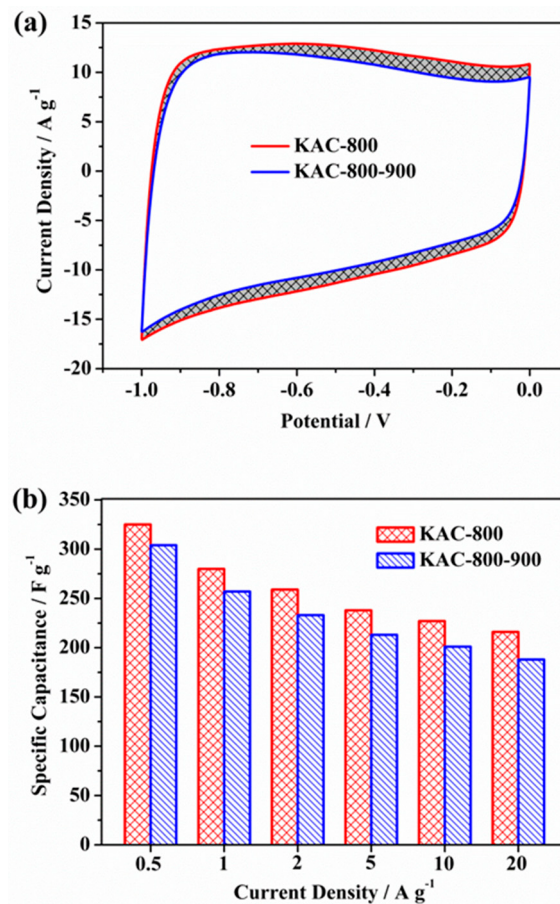


Figure 6. (a) Comparison of CV curves of KAC-800 and KAC-800-900 at the scan rate of 50 mV s⁻¹; (b) specific capacitances of KAC-800 and KAC-800-900 as a function of the current densities.

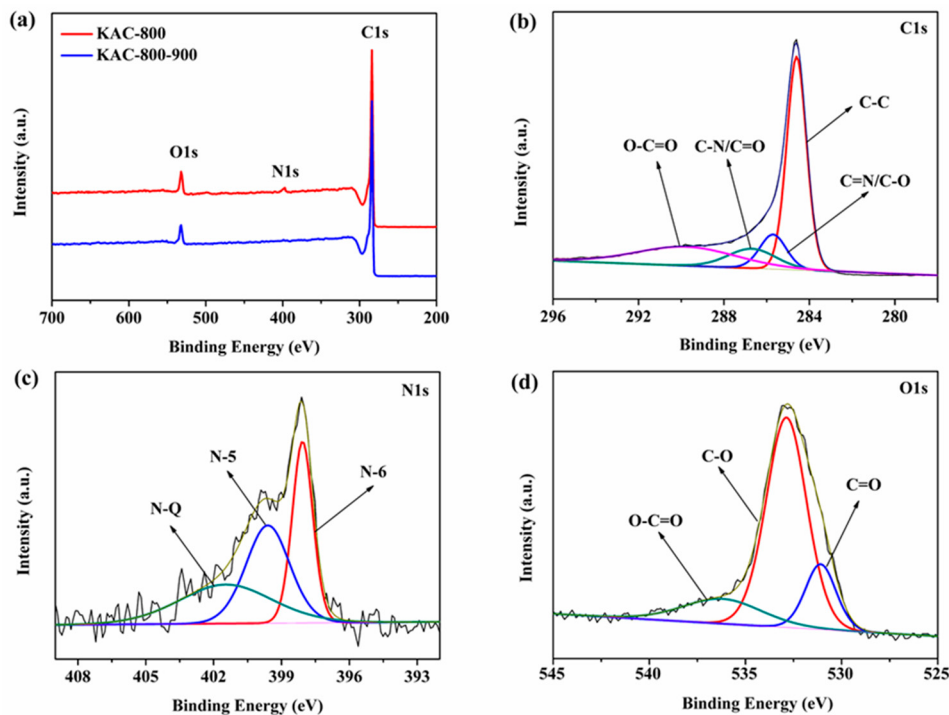


Figure 7. (a) XPS survey spectra of KAC-800 and KAC-800-900; (b) C1s spectrum of KAC-800; (c) N1s spectrum of KAC-800; (d) O1s spectrum of KAC-800.

The nitrogen content variation across samples was confirmed by Raman spectra (Figure 8a). Two characteristic peaks centered at approximately 1354 and 1596 cm^{-1} sequentially belong to the disordered and graphitized carbon [35]. The peak intensity ratios of the D and G bands (I_D/I_G) of KAC-800 and KAC-800-900 are 1.40 and 1.30 (Table S3), respectively. The position, intensity (relative to the G-band) and broadening of the D band depend on the nature of impurities and functional groups, and the type of disorder. The relatively lower D/G intensity ratio for KAC-800-900 can also give shape to a reduced nitrogen content and simultaneously a higher carbon graphitization degree. The consistent conclusion can further be espoused by thermo-gravimetric experiment. From the DTA (Figure 8b) and DTG curves (Figure S5), the KAC-800-900 shows the higher temperature of exothermic peak under the air flow, pinpointing its higher crystallization extent [36].

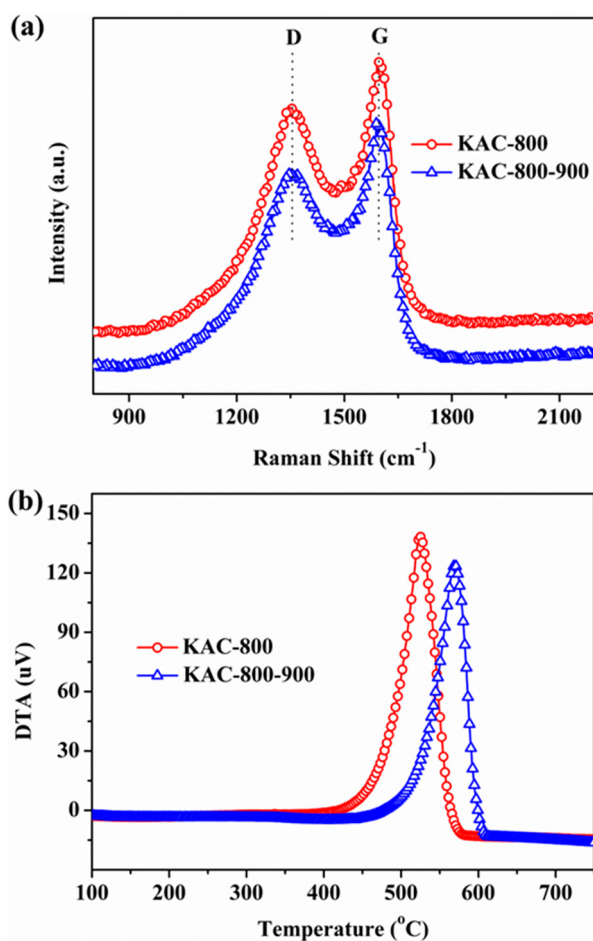


Figure 8. (a) Raman spectra and (b) DTA curves of KAC-800 and KAC-800-900.

Supercapacitive properties for all porous carbon electrodes were further probed by electrochemical impedance spectroscopies (EIS) characterization and the corresponding Nyquist plots are supplied in Figure 9. In the low-frequency region, the Nyquist plots of KAC-800 and KAC-800-900 describe the typical features of EDLCs with the nearly vertical lines, denoting an ideal capacitive behavior and low electrolyte diffusion resistance in the electrode material [37]. KAC-800 owns a more vertical straight line along the imaginary axis, articulating its lower electrolyte diffusion resistance than the KAC-800-900 electrode [38]. The inset in Figure 9 sketches a magnified high-frequency region for KAC-800 and KAC-800-900. The equivalent series resistance (R_{ESR}) is calculated from x -intercepts with the real axis of the Nyquist plots in the high-frequency region. It can be ascertained that the KAC-800 electrode harbored a lower x -intercept than KAC-800-900, deciphering its higher electrical conductivity and more excellent pore accessibility for electrolyte ions [39]. This could be attributed to the presence of nitrogen-containing functional groups in the KAC-800 that can encourage the wettability and electrical

conductivity and therefore furnish the minimized diffusive resistance to electrolyte ion conveyance [40]. In short, combined with the preceding explorations, our vivid comparison study between KAC-800 and KAC-800-900 does spell out the vital implications that the nitrogen dopant has upon expediting the ion kinetics and ion access to the electrode surfaces during the electrochemical events.

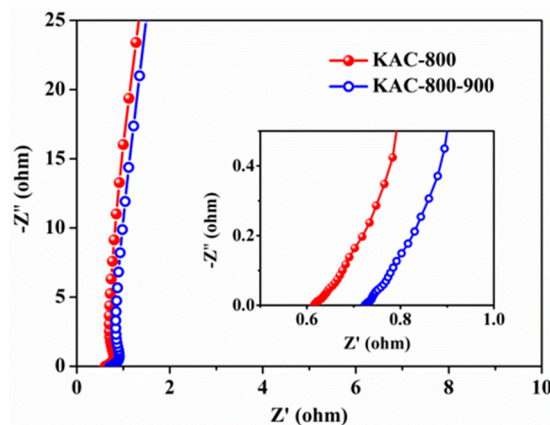
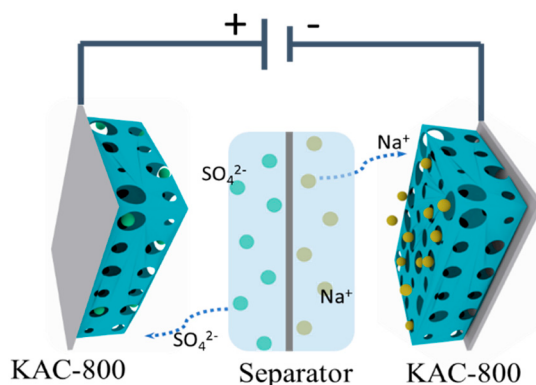


Figure 9. Impedance Nyquist plots of KAC-800 and KAC-800-900 (inset enlarged high-frequency region of Nyquist plots).

3.3. Supercapacitor Performance of KAC-800 Symmetric Device

In order to further demonstrate the actual electrochemical behavior and potential applications of our materials, we assembled two electrode symmetric cell devices based on the KAC-800 electrode in 6 M KOH and 1 M Na_2SO_4 , and its schematic structure is illustrated in Scheme 2. Electrochemical performances of the KAC-800 symmetrical two-electrode system were first studied in the 6 M KOH electrolyte. As offered in Figure 10a, the cyclic voltammetry of the KAC-800 symmetric cell is characterized by a rectangular shape between 0 and 1.0 V in 6 mol L^{-1} KOH solution, which exemplifies the ideal electrochemical double-layer capacitive behavior [41]. Furthermore, KAC-800 still assumes a typical rectangular CV curve even at a scan rate as high as 300 mV s^{-1} , which sets forth the efficient charge transfer and electrolyte diffusion inside porous carbon material [32]. The nearly symmetrical triangular form of the GCD curves (Figure 10b) accounts for the impressive charge propagation behavior of the electrolyte ions [42]. Specific capacitances calculated from GCD curves at various current densities of the cell are presented in Figure 10c. The calculated largest specific capacitance of the cell is 47 F g^{-1} at the current density of 0.5 A g^{-1} . The Ragone plot for the KAC-800 symmetric cell in 6 mol L^{-1} KOH electrolyte can be found in Figure 10d. The specific energy density of the two-electrode cell approaches 6.5 Wh kg^{-1} with a power density of 250 W kg^{-1} under a current density of 0.5 A g^{-1} , which is superior to commercial devices ($<3 \text{ Wh kg}^{-1}$) [43,44].



Scheme 2. Illustration of the assembled symmetric capacitor using KAC-800 as electrode materials.

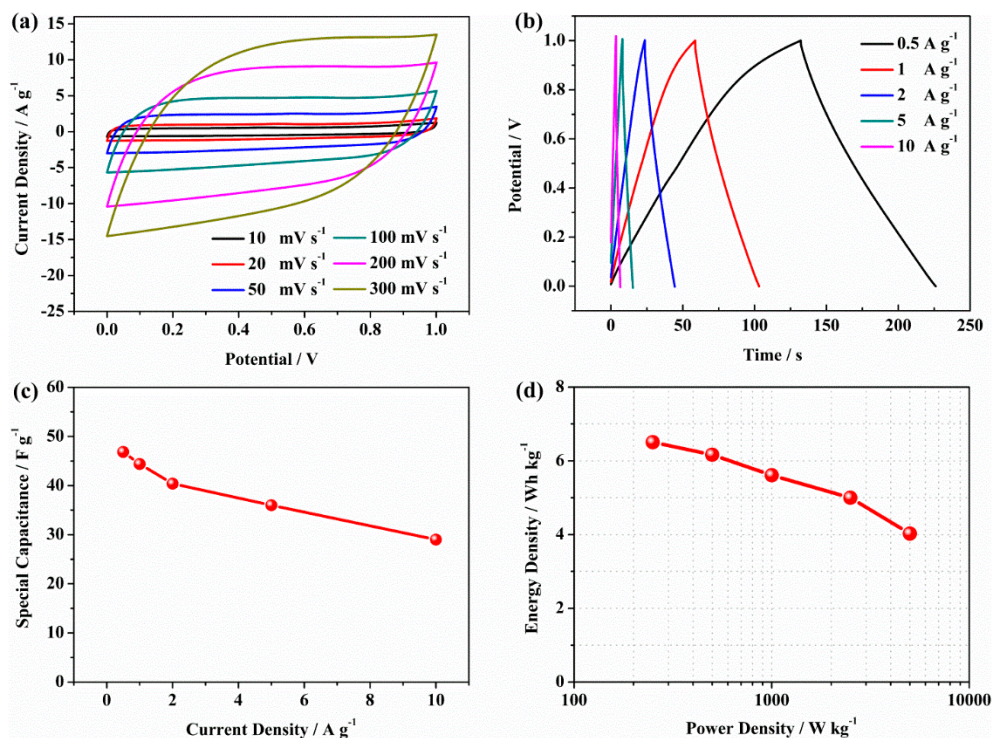


Figure 10. Electrochemical performances of the KAC-800 symmetric cell measured in 6 M potassium hydroxide (KOH) electrolyte: (a) CV curves at different scan rate; (b) GCD curves at various current densities; (c) capacitances of KAC-800 electrode at various current densities; (d) Ragone plot of KAC-800.

KAC-800 also bestows the fascinating supercapacitor performance in 1 mol L⁻¹ Na₂SO₄ electrolyte. The neutral Na₂SO₄ electrolyte has been extensively scrutinized for electrical double-layer capacitors by virtues of its environmental friendliness, cost-effectiveness, and great ease to construct relative to the organic solution [45]. On the other hand, it is endowed with a higher operating voltage than those of acid and alkali solutions, and thus the high energy density can come true for supercapacitors [46]. Therefore, the KAC-800 symmetric supercapacitors were further canvassed in 1 M Na₂SO₄ electrolyte. Figure 11a pictures CV curves of KAC-800 symmetric supercapacitor at different potential windows at the scan rate of 50 mV s⁻¹. The CV curves of the supercapacitor still sustain a rectangular-like feature when the operational voltage extends to a very high value of 1.8 V, explaining the ideal capacitive behavior and striking reversibility. However, the anodic current undergoes a dramatic increment at the voltage of 2 V due to hydrogen and oxygen evolution reactions [46]. Accordingly, the KAC-800 symmetric supercapacitor experiences a detail examination in the voltage range of 0–1.8 V. The CV curves of the symmetric cell monitored at the different scan rates from 10 to 300 mV s⁻¹ are shown in Figure 11b. The rectangular CV curve of the as-assembled KAC-800 supercapacitor can be maintained even at a high scan rate of 300 mV s⁻¹, emphasizing an ideal electrochemical capacitive behavior with the rapid ion diffusion [47]. Figure 11c displays GCD curves of the symmetric cell at the varying current densities from 0.5 to 10 A g⁻¹. The linear and symmetrical GCD profiles substantiate that the as-fabricated KAC-800 symmetric supercapacitor features the excellent electrochemical reversibility. The symmetric supercapacitor achieves a maximum capacitance of 52 F g⁻¹ at 0.5 A g⁻¹ (Figure 11d). The inset in Figure 11d shows a Ragone plot. The results discovered that the symmetric cell delivers the highest energy density of 23.5 Wh kg⁻¹ with a power density of 450 W kg⁻¹, and retains 12.5 Wh kg⁻¹ at 9000 W kg⁻¹, interpreting an ultrafast ion/electron diffusion and remarkable energy/power rating behavior. Noteworthy, the maximum energy density of 23.5 Wh kg⁻¹ here notably exceeds other carbon-based symmetric supercapacitors found in the literature [45–48].

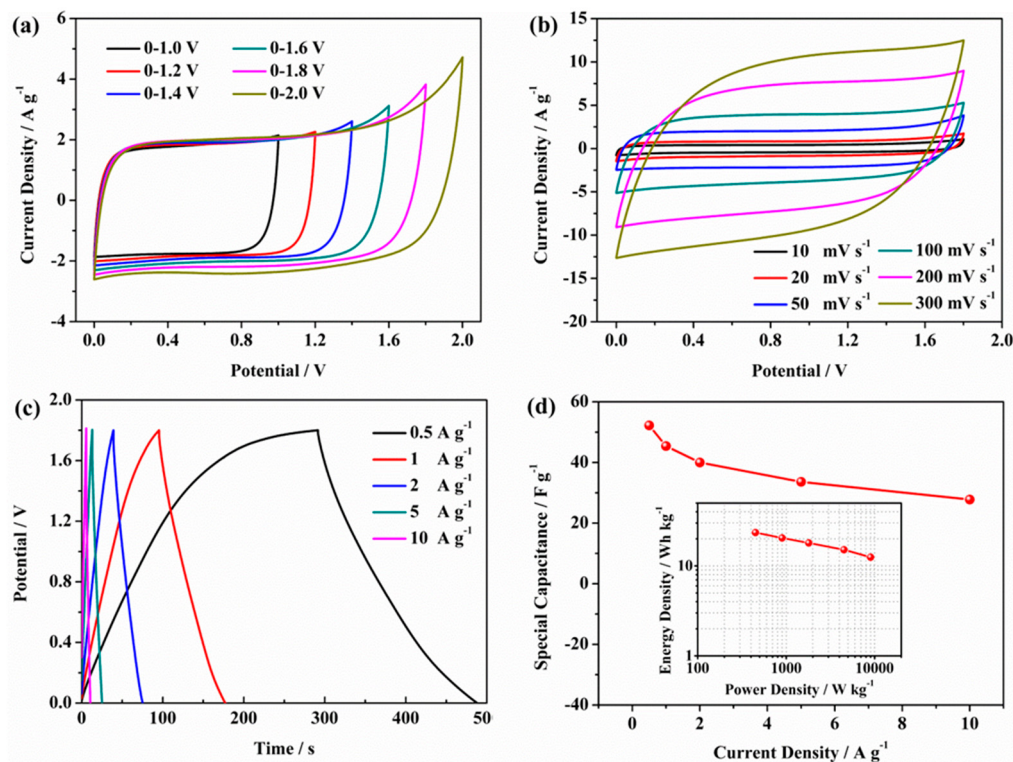


Figure 11. Electrochemical measurements of the as-assembled KAC-800 symmetric supercapacitor in 1 M Na₂SO₄ electrolyte: (a) CV curves of the cell operated in different operation voltages at a scan rate of 50 mV s⁻¹; (b) CV curves of the cell at various scan rates. (c) GCD curves of the cell at various current densities; (d) capacitances of KAC-800 electrode at various current densities. The inset shows the Ragone plot.

Hence, in light of the above discussions, it can be seen that the KAC-800 electrode material possesses superior electrochemical properties, which can be attributable to a synergic collaboration of its high SSA, uniform PSD, and proper nitrogen content. Profoundly, these well-regulated textural properties can facilely come into reality just through pyrolyzing the common biomass resource of the anthracite. Our study here offers an attractive arena or tenet toward metamorphosing the low-value biomass into a more precious “treasure” desirable for nascent electrochemical energy storage sectors.

4. Conclusions

In summary, we demonstrate a tractable KOH activation route toward the scalable production of the porous N-doped carbon from naturally available and low-cost anthracite biomass as electrode materials for supercapacitors (SCs). This synthetic approach can result in the functionalized carbon materials with some pivotal superiorities: (1) a good textural development (for example, colossal BET surface areas up to 2814 m² g⁻¹ and pore volumes as high as 1.531 cm³ g⁻¹), (2) multiscale porosity (mixture of predominant micropore of 1–2 nm and small-sized mesopores of 2–4 nm), and (3) proper nitrogen dopant content (2.77 at%). The optimal porous doped carbon can impart good supercapacitive performance with a great specific capacitance of 325 F g⁻¹ at 0.5 A/g, decent rate capability, and stable cyclic lifetime even after 5000 consecutive cycles at 10 A g⁻¹ (92% capacity retention). As a result, the assembled symmetric SC in 1 mol L⁻¹ Na₂SO₄ aqueous electrolyte can well work at 1.8 V to deliver a superior energy density of 23.5 Wh kg⁻¹ at a power density of 450 W kg⁻¹ and to still maintain 12.5 Wh kg⁻¹ at 9000 W kg⁻¹. All characterizations verify that the greatly improved electrochemical behavior can benefit from excellent mass/charge transportation and ample heteroatom active sites. The wieldy one-step KOH activation technique can act as a potential strategy for the massive production of anthracite-derived multifunctional nanocarbon materials for a cathodic

cascade of energy storage systems where the homogeneous small pores and proper dopants do carry great clout with energy storage mechanism.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3417/10/3/1081/s1>, Figure S1: PSD of samples, Figure S2: N₂ adsorption-desorption isotherm of KAC-800-900, Figure S3: PSD of KAC-800-900, Figure S4: XRD pattern of KAC-800-900, Figure S5: DTG curves of KAC-800 and KAC-800-900, Table S1: The proximate analysis and element analysis data of anthracite, Table S2: Textural properties of KAC-800-900 (Calculated total surface area S_{BET} , total pore volume V_T , average pore diameter d_M), Table S3: Textural properties and chemical composition of KAC-800 and KAC-800-900 (atomic percent of elements obtained from XPS analysis).

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