Self-Activation of Cellulose: A New Preparation Methodology for Activated Carbon Electrodes in Electrochemical Capacitors

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Abstract

Current synthetic methods of biomass-derived activated carbon call for a high temperature pyrolysis followed by either a chemical or physical activation process. Herein, we report a simple one-step **annealing** synthesis yielding a high surface area cellulose-derived activated carbon. We discover that simply varying the flow rate of Argon during pyrolysis enables ‘self-activation’ reactions that can tune the specific surface areas of the resulting carbon, ranging from 98 m²/g to values as high as 2600 m²/g. Furthermore, we, for the first time, observe a direct evolution of H₂ from the pyrolysis, which gives strong evidence towards an in situ self-activation mechanism. Surprisingly, the obtained activated carbon is a crumbled graphene nanostructure composed of interconnected sheets, making it ideal for use in an electrochemical capacitor. The cellulose-derived nanoporous carbon exhibits a capacitance of 132 F g⁻¹ at 1 A g⁻¹, a performance comparable to the state-of-the art activated carbons. This work presents a fundamentally new way to look at the synthesis of activated carbon, and highlights the importance of a controlled inert gas flow rate during synthesis in general, as its contributions can have a very large impact on the final material properties.

Keywords

Pyrolysis; Cellulose; flow rate; self-activation; electrochemical capacitor

Introduction

Annually around 50 million tons of forestry residues are produced as ‘waste’ in the U.S. alone [1]. This causes severe environmental concerns, such as a greater risk of forest fires and greenhouse gas emission [2]. While the biomass residues can be processed into valuable products, e.g., biofuels, high overhead costs, such as transportation from forest to processing sites, greatly decrease its economic viability [3-5]. Thus, it is of high urgency to discover scalable and affordable chemical methods that can convert biomass into valuable materials of even higher values. Along this line, activated carbon (AC) is one of the most promising materials that can be synthesized from biomass. With desirable properties, such as high surface area, chemical inertness, and good electrical conductivity, AC is a critical component for a plethora of applications, including energy storage [6-8], catalysis [9, 10], water/air purification [11-13], and gas storage [14, 15].

Currently, there are primarily two routes to synthesize ACs from biomass: “physical” activation and chemical activation. Physical activation requires two steps, where the first is pyrolysis and the following step is activation through gaseous etchants, e.g., CO_2 or H_2O steam [16-28]. In chemical activation, a mixture of biomass and activation reagents, such as KOH , $\text{B}(\text{OH})_3$, H_3PO_4 , NaOH , or ZnCl_2 is pyrolyzed before washing of the resulting carbon following activation [29-41]. Both physical and chemical activation methods lead to environmental consequences, and they involve multiple steps to obtain the final products, which drives the cost high. Thus, fundamentally more efficient methods are highly desirable.

Recently Luo *et al.* first discovered a one-step activation of cellulose under NH_3 gas, where occur the simultaneous pyrolysis, activation and nitrogen doping [42]. However, NH_3 gas is corrosive and relatively expensive. The question instead is whether AC can be prepared through a simple control of the pyrolysis parameters of biomass, instead of consuming either chemical or physical activation reagents. The influence of pyrolysis parameters such as flow rate of inert gas, pyrolysis temperature and reaction duration on the synthesis of biochar, was investigated Luo *et al.* [43, 44] who

were able to optimize the surface area up to $778 \text{ m}^2 \text{ g}^{-1}$; though it should be noted that those reactions consumed CO_2 gas—a physical activation agent. Similar studies on the effect of pyrolysis parameters obtain surface areas of $519 \text{ m}^2 \text{ g}^{-1}$ and $707 \text{ m}^2 \text{ g}^{-1}$ [45, 46]; but again the former work utilized a steam activation, while the latter study did not change the flow rate. While these early studies demonstrate that the high surface area, porous biochar can be synthesized through control of the pyrolysis parameters, they still were not able to demonstrate a one-step self-activation that produces a surface area comparable to traditional ACs.

Herein, we report that one-step pyrolysis of cellulose results in carbon surface area as high as $2600 \text{ m}^2/\text{g}$. Furthermore, we attribute the high surface area to the reaction between H_2O released during carbonization and the derived carbon. We identify that the flow rate of the inert gas determines the H_2O residence time and subsequently the levels of self-activation: a high flow rate prevents the self-activation due to a low residence time, while a low flow rate enhances the self-activation.

Materials and Methods

Preparation of Activated Carbon

We use filter paper (Whatman™ Type 1) comprising pure cellulose as the precursor. The pyrolysis is conducted under Argon at 1100°C for 2 h in the middle of a tube furnace with the inner diameter of 4.45 cm. The furnace is purged under a high flow rate of Argon for 30 min, before being switched to a desired flow rate. Flow rates of 10, 25, 50, 100 and $200 \text{ cm}^3 \text{ min}^{-1}$ (CCM) are used. We refer to the samples according to respective flow rates, e.g., C-200 for the sample obtained under 200 CCM of Argon.

Material Characterizations

Brunauer-Emmett-Teller (BET) surface area and Density Functional Theory (DFT) pore volume calculations are based on N_2 sorption measurements on a Micromeritics TriStar II 3020 analyzer. XRD patterns are obtained by a Rigaku Ultima IV Diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). Raman spectra are collected using a HR 800 LabRam HORIBA JOBIN YVON system with a 532.02 nm laser

source. Scanning Electron Microscopy (SEM) images are recorded through a FEI Quanta 600 SEM. Transmission Electron Microscopy (TEM) images are collected with a FEI Titan 80-300 TEM. X-ray photoelectron spectroscopy (XPS) measurements are conducted on a Physical Electronics Quantera ESCA Microprobe with a focused Al K α X-ray (1486.6 eV) source for excitation. The X-ray beam is a 25 W, 100 μ m X-ray beam spot at the sample. The ion gun used is a standard Quantera ion gun, and the sputtered depth profiles are acquired using a 1 KeV argon-ion beam rastered over a 3 mm x 3 mm area; and the binding energy scale is calibrated using the Cu 2p_{2/3} feature at 932.62 (+/-) 0.05 eV and Au 4f at 83.96 (+/-) 0.05 eV. Elemental analysis is conducted by a commercial company, Elemental Analysis Inc. Thermogravimetric Analysis (TGA) is conducted on a TA Instruments SDT-Q600 thermal analyzer. During TGA, the samples are heated in a 70- μ l alumina crucible under ultra-high pure Argon (50 CCM) from room temperature to 1100 °C at a ramp rate of 5 °C min⁻¹. The SDT-Q600 is also equipped with a mass spectrometer (MS) for detecting evolved gaseous species. Selected gaseous species, including H₂, H₂O, CO, and CO₂, are monitored during cellulose pyrolysis.

Characterization of Activated Carbons in Electrochemical Capacitors (ECs)

The electrodes are prepared by mixing 80wt% activated carbon, 10wt% carbon black, C-45 (TimCal) and 10wt% poly-1,1-difluoroethene (PVDF) binder in n-methyl-2-pyrrolidinone (NMP). The resulting paste is painted onto a current collector of stainless steel mesh and dried at 60°C in a vacuum oven. The active mass loading of the electrodes is ~1 mg cm⁻². Two-electrode capacitors are assembled in 2032 coin cells containing an aqueous electrolyte of 6 M KOH. Galvanostatic cycling is conducted on a Maccor 3000 at 25°C at a current rate of 1 A g⁻¹. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectra (EIS) are obtained on a Bio-logic EC Lab VMP-3 under ambient conditions. Specific capacitance is obtained from data obtained during galvanostatic cycling using the Eq. 1

$$C_s = \frac{4I \cdot \Delta t}{m \cdot \Delta V} \quad Eq. (1)$$

where I is the current rate used and m is the mass of the both electrodes. The equivalent series resistance (ESR) is obtained through Eq. 2

$$R_{ESR} = \frac{V_{drop}}{2I} \quad Eq. (2)$$

whereby V_{drop} is the voltage drop at the onset of discharge and I is the current rate used. Lastly electrochemical impedance spectra (EIS) of the symmetric ECs were conducted from 200 kHz to 10 mHz.

Results and Discussion

The impact of Argon flow rate is evident from the N₂ sorption measurements of the resulting nanoporous carbon (**Figure 1, Table 1**). As the flow rate decreases, the N₂ absorption volume steadily increases. Using a low flow rate of 10 CCM results in a specific surface area of as high as 2,600 m² g⁻¹ as opposed to only 98 m² g⁻¹ when a high rate of 200 CCM is used. Performing a linear regression analysis of specific surface area and pore volume as a function of Argon flow rate yields an R² of 0.961 and 0.965, respectively, revealing a strong inverse correlation (**Supplementary Figure S1 & S2**). Both linear regressions are performed on logarithm-transformed scales of flow rates. The high surface area and a short reaction time here are in sharp contrast to the CO₂ activation of carbon that requires long reaction time, e.g., more than 15 hours, in order to yield a surface area of 2,400 m² g⁻¹ (**Supplementary Figure S3**). The pore size distributions show that the greatest portion of pore volume is attributed to pores between 2 nm and 20 nm (mesopores), followed by pores greater than 20 nm ('macropores'), and pores of less than 2 nm (micropores) (**Table 1 and Figure 1c**). Materials obtained at lower flow rates exhibit a much more even distribution of pores, which accounts for the switch from type I N₂ sorption isotherm at high flow rates to type I/IV isotherms at low flow rates. Lastly, in **Figure 1d**, we see that there is a linear correlation between the increase in pore volume and flow rate for all three types of pores; performing a linear regression of incremental pore volume versus flow rate yields R² values of 0.96 for the micropores, 0.97 for the mesopores and 0.87 for the 'macropores' (**Supplementary Figure S4**). The results show that increases in porosity due to a lower flow rate in all types of pores are nearly linear as the flow rate is lowered.

Argon Flow Rate (CCM)	BET Surface Area ($\text{m}^2 \text{g}^{-1}$)	DFT Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Pore Size Distribution volume ($\text{cm}^3 \text{g}^{-1}$)			Thickness in (002) direction	Empirical R Value	I_D/I_G Value	% Yield
			< 2 nm	2 nm to 20 nm	> 20 nm				
10	2602	2.110	0.0435	1.665	0.562	2.82	1.22	1.13	1.6
25	1637	1.156	0.0131	0.453	0.110	3.06	1.23	1.09	6.7
50	598	0.453	0.0025	0.075	0.016	3.39	1.48	0.99	13.3
100	337	0.226	0.0018	0.046	0.015	3.46	1.45	0.94	15.2
200	98	0.062	0.0009	0.021	0.012	3.57	1.82	0.95	16.7

Table 1. Results of BET surface area and DFT pore volume, as well as XRD and Raman results of the carbon materials obtained at different flow rates.

Figure 1. a) N₂ sorption isotherms of different activated carbons, b) Dual plots of surface area and pore volume values versus Argon flow rates. c) Pore size distribution plot of the carbon materials d) Comparison of incremental volume of micropores, mesopores and macropores for the different activated carbon materials.

Following the N₂ sorption measurements, we further characterized the structures of the obtained activated carbons. All of the obtained carbon samples exhibit an amorphous atomistic structure by

displaying broad (002) and (100) peaks at 2θ angles of 23° and 43° , respectively. The measured d-spacings of (002) planes of the respective carbon samples do not vary much upon different flow rates, with most around 0.39 nm. However, the short-range order along the *c*-axis of the synthesized carbons varies greatly upon different Ar flow rate as evident from the XRD profiles. Carbons obtained at high flow rates exhibit better resolved (002) peaks than those prepared at low flow rates (**Figure 2a,c**). Calculation by the Scherrer equation allows us to deduce the average thickness of the nanodomains along the *c*-axis, L_c [47-49]. Dividing the nanodomain thickness by the d-spacing estimates the average number of graphene layers, which decreases from 3.6 to 2.8 when the flow rate decreases from 200 to 10 CCM (**Table 1**). When a linear regression of number of graphene layers vs. flow rate is performed, we obtain an R^2 value of 0.948, thereby showing that carbon nanodomains are thinned at low flow rates during pyrolysis (**Supplementary Figure S5**). The degrees of order along the *c* axis can be analyzed by *R* calculations as well; *R*, an empirical parameter defined by Dahn *et al.*, measures a ratio of (002) peak intensity, *B*, compared to the background, *A*, at the same diffraction angle (**Supplementary Figure S6**) [50]. This measurement allows quantifying the degrees of short-range order in an amorphous carbon, with higher *R* values implying a better degree of order. The *R* values obtained correlate well with the nanoporosity induced in carbon, with high-surface-area carbon having an *R* value of 1.2 but low-surface-area carbon exhibiting an *R* value greater than 1.8 (**Table 1**). Performing a linear regression analysis on flow rates vs. *R* values and logarithm transformed data yields a R^2 value of 0.817 (**Supplementary Figure S7**).

We further investigate the microstructure of the resulting carbons by TEM. As **Figure 3a** shows, C-200 with a specific surface area of $98 \text{ m}^2 \text{ g}^{-1}$ contains randomly arranged curved graphene layers, described by the “house-of-cards” model [51-54]. On the other hand, C-10, also composed of curved graphene sheets, exhibits a much lower packing density of carbon sheets (**Figure 3b**). This observation corroborates the XRD results that carbon activation occurs at low flow rate by thinning the carbon nanodomains along the *c* axis. SEM imaging is able to show some evidence of increased macroporosity

when a low flow rate is used as opposed to high flow rate ones—though the scale of observation is too large to observe any features of the microstructure (**Supplementary Figure S8**).

Raman spectroscopy provides further structural insights of the amorphous carbon materials, particularly, the disorder degree in the graphene sheets (ab plane). A higher I_D/I_G , intensity of D-band at 1340 cm^{-1} over G-band at 1580 cm^{-1} that correspond to the defected sp^2 and intact sp^2 graphene, respectively, indicates a lower intactness of graphene. The I_D/I_G ratios of the resulting carbon prove to be inversely correlated to the flow rate as well, with a maximum ratio of 1.10 at 10 CCM and a minimum ratio of 0.94 at 200 CCM (**Figure 2b,c**). It is evident that at a low flow rate, more defects in graphene sheets are generated. Considering that both the specific surface area/pore volume and I_D/I_G ratios inversely correlate with the flow rate, a linear regression is performed for I_D/I_G ratio as a function of both BET surface area and DFT pore volume. Both linear regressions show a strikingly high degree of correlation, with R^2 values being of 0.971 and 0.940. This implies an important message that porosity generation does occur in graphene planes. (**Supplementary Figure S9 & S10**).

Up to this point, from the XRD, TEM and Raman results, it is evident that activation of the resulting carbon does occur through two distinct routes: and creating defects on the graphene sheets along ab plane.

Figure 2. a, b) XRD patterns and Raman spectra of cellulose pyrolyzed for 2 h under different flow rates, c) Dual plot of the empirical R value and I_D/I_G ratios vs. flow rate of Argon.

Figure 3. Typical TEM images showing the carbon microstructures of a) C-200 b) C-10. Both images show the randomly arranged curved graphene sheets and domains inside the samples.

To elucidate the mechanism behind the inverse correlation of the activation process and the Argon flow rates, we monitored the evolved H_2 , H_2O , CO and CO_2 gases during pyrolysis via TGA-MS [55-60]. Although there are other larger volatile molecules possibly generated from cellulose pyrolysis, these four molecules are used here as markers to help understand the activation mechanism. As **Figure 4a** shows, the majority of the weight loss during cellulose pyrolysis occurs between 250 °C and 400 °C while the elimination of H_2O along with minor evolution of CO and CO_2 is observed. This process is often referred to as a primary reaction in cellulose pyrolysis. An important question to be answered here is how this pyrolysis process affects the overall physicochemical properties of the resulting carbon. Is the weight loss incurred from 250 °C and 400 °C inconsequential, or is it the sole reason for the self-activation reactions?

To answer this question, we pretreated cellulose at 450 °C and 600 °C for 6 h, respectively, under Argon at a very high flow rate of 200 CCM. The pre-treatment aims to completely remove the ‘possible’ activation reagents generated at relatively low temperatures before the following high-temperature investigation. Furthermore, the high flow rate guarantees that little self-activation reactions take place during the pre-treatment. The two obtained samples are referred to as P-450 and P-600. After the pretreatment, P-450 and P-600 are further pyrolyzed at 1100 °C for 6 h in under Argon at 10 CCM, resulting in surface areas of 1500 m² g⁻¹ and 730 m² g⁻¹, respectively (**Supplementary Figure S11**).

The above results provide two important insights. Firstly, it confirms that the species released below 450 °C and between 450 °C to 600 °C do contribute to the activation, considering that when a flow rate of 10 CCM was used for the entire pyrolysis process, a final surface area of 2,600 m² g⁻¹ was obtained. Secondly, it is evident that above 600 °C there are still activation reagents released during cellulose pyrolysis, considering that C-200 sample has a final surface area of 98 m² g⁻¹. Activation at above 600 °C is supported by the TGA of P-600 as a significant percentage of weight loss occurs at temperatures beyond 600 °C (**Figure 4c & 4d**). At pyrolysis temperatures below 600 °C, it is known that cellulose polymer chains are dehydrolyzed and subsequently decomposed into a plethora of volatile molecules, also referred to as bio-fuels or bio-oils [61]. Such liquification reactions peak at around 550 °C and are mostly completed by 600 °C [62-64]. At temperatures greater than 600 °C, the pyrolysis process begins to transition towards the release of smaller non-condensable gasses, such as H₂, H₂O, CO and CO₂ [65]. With this in mind, we thus propose that there are two possible self-activation reactions which can happen at higher temperatures.

The occurrence of these two activation reactions are supported by the TGA-MS results, as they show a stable evolution of H₂O at higher temperatures with much higher pressure than CO and CO₂. The MS results imply that the removal of residual hydrogen and oxygen atoms may form H₂O at a wide range of temperatures during the pyrolysis process. Furthermore, there is a distinct peak of H₂ evolution from 750

°C to 800 °C (**Figure 4b, c**). This is consistent to the calculated temperature of 707 °C, whereby the Gibbs free energy of the syngas formation reaction (Eq. 3) turns negative and thus the reaction becomes spontaneous. The H₂ peak at above 700 °C may explain what the activation reaction is at high temperatures. Furthermore, the high H₂ pressure leads to yet another possible activation reaction:

Despite the possibility of self-activation via Eq. 4 & Eq. 5, it is more likely that the syngas formation plays the primary role due to the vastly higher pressure of H₂O.

Figure 4. a) TGA and MS profiles of a) cellulose, b) sample pre-treated at 450 °C, c) Sample pre-treated at 600 °C d) IR spectra of carbon samples pyrolyzed at 450 °C, 600 °C and 1100 °C

IR spectra provide insights on the activation mechanism as well. As **Figure 4d** shows, the pyrolysis at 1100 °C results in a very pure carbon, with almost no signals from oxygen-containing functional groups. Conversely, P-450 exhibits peaks from a wide range of groups, including C=O and

C-O, and weaker signals of substituted aromatic rings, e.g., aldehydes and carboxylic acids. Similar C=O and C-O peaks still exist after a pre-treatment at 600 °C though the signals are considerably weaker. When integrating the IR and TGA/MS results, it is evident that as the pyrolysis temperature increases, the removal of oxygen and hydrogen groups results in the release of H₂O that activates carbon, thus forming H₂ as a by-product.

When a low flow rate is used, evolved activation gas molecules, e.g., H₂O, remain in the tube furnace for a longer time period, increasing the likelihood of the reaction in Eq. 3. The concept of using a low flow rate, and its consequence of inducing self activation can better be understood through the calculation of residence times (τ) of gas molecules in the reaction chamber. The residence time can be estimated through the equation

$$\tau \text{ (min)} = \int_{x_1}^{x_2} \frac{A_i}{F_0} \cdot \frac{T_{furnace}(x)}{T_{room}} dx \quad \text{Eq. (6)}$$

where τ is the residence time in min, A_i is the cross-sectional area of the reaction chamber in m², F_0 is the inlet flow rate in m³ min⁻¹, $T_{furnace}$ and T_{room} are the temperatures in Kelvin, and x_1 and x_2 are boundaries of the alumina crucible holding the filter paper. It is evident that the residence time is inversely proportional to the flow rate. Since the flow of Argon replaces the self-activation agents, such as H₂O and CO₂, it is reasonable to believe that these self-activation agents have very similar residence time as the Argon molecules flowing through the reaction chamber. Thus, a low flow rate of Argon results in higher residence times of self-activating agents, thereby increasing the likelihood of a self-activation reaction. As we can see from **Figure 5** the residence times for lower flow rates are 10 to 20 times greater than those of higher flow rates; whereas the residence time at 1100 °C for a flow rate of 200 CCM is of only 12 seconds, it jumps to nearly 4 minutes when the flow rate is lowered to 10 CCM.

Figure 5 Residence times (τ) as obtained through the use of Eq. 6

We investigated the electrochemical properties of the C-10 of a surface area of $2,600 \text{ m}^2/\text{g}$ in symmetrical electrochemical capacitors (ECs). Cyclic voltammetry measurements are conducted at scanning rates of 20, 200, 500 and $1,000 \text{ mV s}^{-1}$. As shown in **Figure 6a**, C-10 exhibits excellent high-rate capacitive behavior as the CV profile retains its rectangular shape even at a scanning rate of 1000 mV s^{-1} . From the EIS results, the Nyquist plot shows an intercept at the real impedance (Z') of 0.6Ω , indicating a very low equivalent series resistance (ESR). An elongated ‘semicircle’ can be attributed to the widely distributed pore sizes in the structure. The Nyquist plot was simulated using two RC circuits connected in series and a restricted diffusion element M, as shown in **Supplementary Figure S12**. Galvanostatic charge/discharge of C-10 EC cells at a current rate of 1 A g^{-1} yields very symmetrical profiles, with a low voltage drop when switching from charge to discharge, thus corroborating the low

ESR value seen from EIS. From the charge/discharge profiles, we observe a specific capacitance of 132 F g⁻¹, which is well retained at over 100 F g⁻¹ when the current rate is increased to 10 A g⁻¹ (**Figure 6c**). After 6,000 cycles, a specific capacitance of 124 F g⁻¹ remains, representing a 94% retention (**Figure 6d**). Despite the much more straightforward and inexpensive preparation, the performance of the nanoporous carbon from direct pyrolysis of cellulose is better than the conventional AC that is formed by activating commercially available petroleum-derived carbon by CO₂. The CO₂ activated carbon, which was measured to have a specific surface area of 2,400 m² g⁻¹ only exhibits a capacitance of 100 F g⁻¹ at 1 A g⁻¹ ¹(**Supplementary Figure S13**).

Figure 6 a) CV curves of ECs with voltage scanning rates ranging from 20 mV s⁻¹ to 1,000 mV s⁻¹. b) Nyquist plot of a capacitor assembled with C-10 as electrodes. c) Galvanostatic charge/discharge profiles at a current rate ranging from 1 A g⁻¹ to 10 A g⁻¹. d) Galvanostatic cycling at a current rate of 1 A g⁻¹.

Conclusion

We demonstrate that high-surface-area nanoporous carbon can be synthesized in a single step pyrolysis reaction without the use of any chemical or physical activating reagents. We record strikingly linear relationships between the flow rates of Argon in the reaction and key properties of the resulting nanoporous carbon, including specific surface area/pore volume and degrees of short-range order. We identify that the high nanoporosity of the resulting carbon is due to the in-situ activation reactions between the resulting carbon and the gases, e.g., H_2O , that are evolved in situ during pyrolysis of cellulose over a wide range of temperatures. The residence time of evolving gases in the reaction chamber exerts a determining impact on the properties of the resulting nanoporous carbon. Through the use of a low flow rate, we are able to synthesize an AC that demonstrates a specific capacitance of 130 F g^{-1} at 1 A g^{-1} , a performance better than that of conventional ACs that are synthesized through tedious processes. We expect that optimization of this one-step self-activation method will greatly lower the cost of ACs, which may have a profound impact on various fields that heavily rely on ACs. .

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Vitae

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Direct pyrolysis of cellulose under Argon can surprisingly produce nanoporous carbon of surface areas as high as 2600 m²/g. It is the very low flow rate of Argon of 10 CCM during pyrolysis that facilitates the high nanoporosity.