

Cellulose-Derived Supercapacitors from the Carbonisation of Filter Paper

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Advanced carbon materials are important for the next-generation of energy storage apparatus, such as electrochemical capacitors. Here, the physical and electrochemical properties of carbonised filter paper (FP) were investigated. FP is comprised of pure cellulose and is a standardised material. After carbonisation at temperatures ranging from 600 to 1700 °C, FP was contaminant-free, containing only carbon and some oxygenated species, and its primary fibre structure was retained (diameter \approx 20–40 μ m). The observed enhancement in conductivity of the carbonised FP was correlated with the carbonisation temperature. Electrochemical capacitance in the range of \approx 1.8–117 F g⁻¹ was achieved, with FP carbonised at 1500 °C showing the best performance. This high capacitance was stable with > 87 % retained after 3000 charge–discharge cycles. These results show that carbonised FP, without the addition of composite materials, exhibits good supercapacitance performance, which competes well with existing electrodes made of carbon-based materials. Furthermore, given the lower cost and renewable source, cellulose-based materials are the more eco-friendly option for energy storage applications.

Advanced carbon materials are important for the next-generation of energy storage apparatus, including fuel cells, secondary batteries and electrochemical capacitors. Industrial demand for such devices is strong, but present manufacturing techniques raise ecological concerns (i.e., use of toxic materials, etc.). The conversion of biomass into functional carbon materials appears to be an efficient, low cost and environmental friendly alternative to presently used materials for energy storage devices.^[1,2] In addition, control of the macro- and micro-structure of cellulose-derived carbon materials offers routes to-

wards the tailored control of properties known to affect performance, such as material porosity, surface area, and nano-shape (e.g., fibres, sheets, etc.).^[1–3] Previously, natural resources have been investigated as a source of these alternative carbon materials, such as disposable cashmere,^[4] sisal fibre,^[5] filter paper (FP),^[6] wool fibres,^[7] coconut shell,^[8] wood,^[9,10] and honeycomb.^[2] A resource common to laboratories worldwide is FP, and here we consider it as an easily accessible source material for cellulose-derived supercapacitors. FP is a source of pure cellulose with a microfibre structure thought to impart favourable electrochemical properties when carbonised.^[6,11] Moreover, the manufacture of FP is standardised, thus it can act as a reference material for carbonisation–electrochemical studies.

In this work, FP was converted into carbon fibre by thermal treatment (temperature range: 600–1700 °C) and characterised by electrochemical and surface analysis methods. Adjustment of the carbonisation temperature was found to influence the physical and electrochemical properties of carbonised FP (e.g., surface area, conductivity, porosity, etc.). It is shown that FP has outstanding electrochemical performance without the addition of any noncellulose material (i.e., not a composite). From these results, it is clear that FP is a promising green-electrode material for supercapacitor applications.

The morphology of FP samples carbonised at 600, 1000, 1300, 1500 and 1700 °C were characterised by scanning electron microscopy (SEM) as shown in Figure 1. Carbon microfibrils 20 to 40 μ m in diameter comprise all samples. The carbonisation temperature did not change the primary fibre structure significantly, although slight heat-shrinkage was observed at higher temperatures. Sample conductivity was measured using conductive atomic force microscopy (AFM) with bias potential of -1 V.

Figure 2 shows the spectrum of FP modified by different carbonisation temperatures. The magnitude of the current density is represented by a colour scale, with yellow and blue indicating low and high current flow, respectively, and thereby low to high conductivity. As carbonisation temperature increases from 600 to 1700 °C, the area identified as nonconductive (yellow) decays, whilst the conductive area (blue) gradually emerges, and then becomes the dominant colour at higher temperatures. This result shows that higher carbonisation temperatures increase the conductivity of FP samples and that carbonisation at 1500 °C causes most of the FP sample to become conductive.

X-ray photoelectron spectroscopy (XPS) was used to analyse the surface chemical composition of the carbonised FP, as displayed in Figure 3. Only peaks at 285.1 and 532.5 eV can be significantly observed from the spectra, which are assigned as originating from C 1s and O 1s photoelectrons, respectively;

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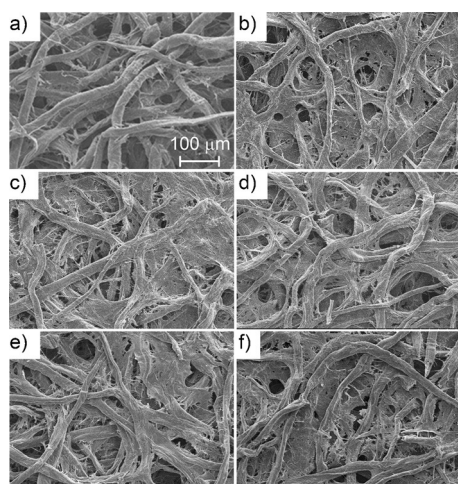


Figure 1. Scanning electron microscopy (SEM) images of filter paper (FP) a) without treatment, and with heat-treatment at b) 600, c) 1000, d) 1300, e) 1500 and f) 1700 °C.

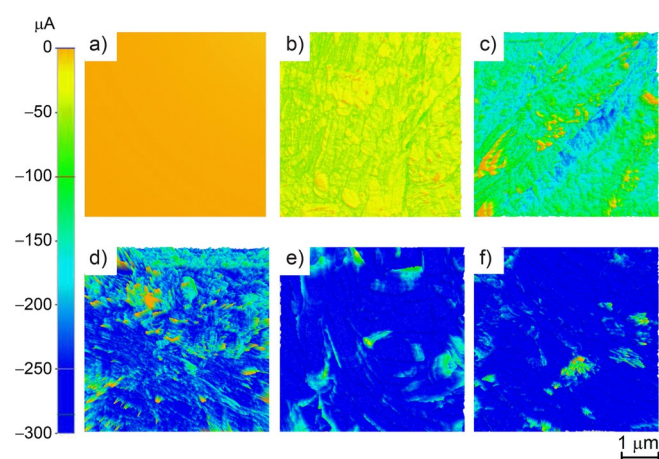


Figure 2. Current flow images of cotton pulp, obtained using atomic force microscopy (AFM), at different carbonisation temperatures: a) raw, b) 600, c) 1000, d) 1300, e) 1500 and f) 1700 °C when -1 V was applied. The corresponding colours for the current flow from $0 \rightarrow 300$ μA are shown in the scale bar on the left.

the ratio of C:O is about 39:1. Since photoelectron signals originating from other elemental core levels are negligible, it suggests that the carbonised FP is contaminant-free and carbon-rich with some O-based groups at the surface.

Cyclic voltammetry (CV) was carried out in a 5 M aqueous KCl solution using an unmodified FP sample (raw) and FP samples carbonised at 600, 1000, 1300, 1500 and 1700 °C. The voltammograms are shown in Figure 4a. Hardly any current flow passes through an electrochemical cell comprised of unmodified FP (—) or 600 °C pretreated FP (---). After carbonisation at 1000 °C (•••••) and 1300 °C (---•), the current density increased gradually, reaching a maximum of approximately 7 A g^{-1} when FP is carbonised at 1500 °C (---). However, carbonisation at 1700 °C (----) decreases current density. Another sample of FP with the highest current density (i.e., 1500 °C) was similarly exposed to a 5 M aqueous KCl solution, and CV

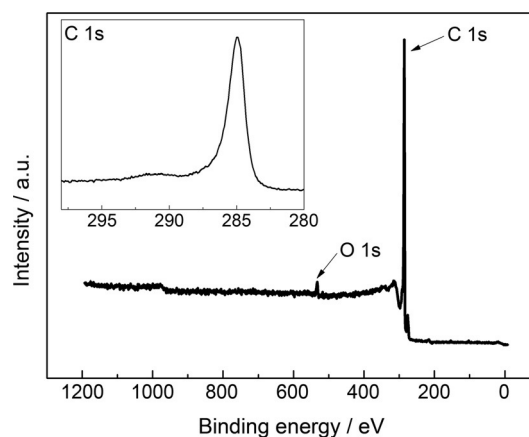


Figure 3. Survey X-ray photoelectron spectroscopy (XPS) spectra of filter paper (FP) carbonised at 1500 °C, with the carbon and oxygen signals indicated. Inset is the narrow spectra of the carbon peak.

was conducted with increasing scan rate from 5 to 100 mV s^{-1} ; the relevant results are shown in Figure 4b. A quasi-rectangular shape along the current–potential axis is observed at all scan rates, suggesting well-defined, electric double-layer capacitive behaviour. Specific capacitance was calculated from the voltammograms (scan rate fixed at 5 mV s^{-1}) of all studied samples and is summarised in Table 1. The specific capacitance increased from 0.07 F g^{-1} to 115.54 F g^{-1} in proportion to increased carbonisation temperature within the range of 0 to 1500 °C. However, the capacitance of the 1700 °C sample dropped to the same magnitude as the 1000 °C sample.

Galvanostatic charge/discharge (GCD) was also used to analyse the electrochemical performance of carbonised FP within a 5 M KCl electrolyte. The experiments were carried out at current density of 1 A g^{-1} at the FP carbonised at different temperatures (raw, 600, 1000, 1300, 1500 and 1700 °C). Representative GCD curves can be found in Figure 5a; the corresponding specific capacitance values determined using GCD are shown in Table 1. The IR drops observed at the raw and 600 °C samples were too fast to be measured, corresponding to extremely low capacitance. Otherwise, the relationship between carbonisation temperature and specific capacitance is the same as that observed by the CV method. According to GCD, use of FP carbonised at 1500 °C leads to the highest specific capacitance

Table 1. Specific supercapacitance (SC) values for filter paper carbonised at different temperatures determined by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD).

Temp [°C]	SC [F g^{-1}] CV	SC [F g^{-1}] GCD
Raw ^[a]	0.07	–
600	3.2	–
1000	24.28	1.83
1300	35.35	28.88
1500	115.54	117.21
1700	22.37	37.08

[a] Raw material was not subjected to elevated temperatures.

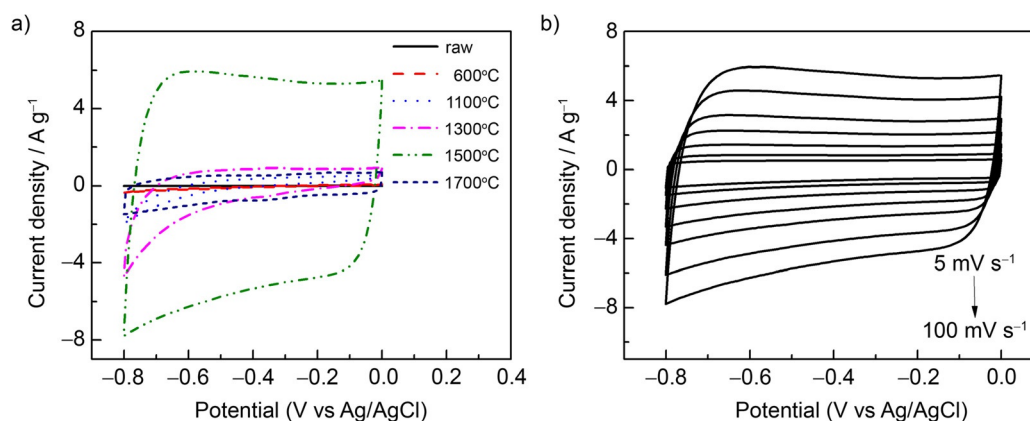


Figure 4. Cyclic voltammograms performed in 5 M aqueous KCl solution with scanning from 0 to -0.8 V: a) raw FP and FP carbonised at different carbonisation temperatures (scan rate: 100 mV s⁻¹); b) FP carbonised at 1500 °C (scan rate: 5 – 100 mV s⁻¹).

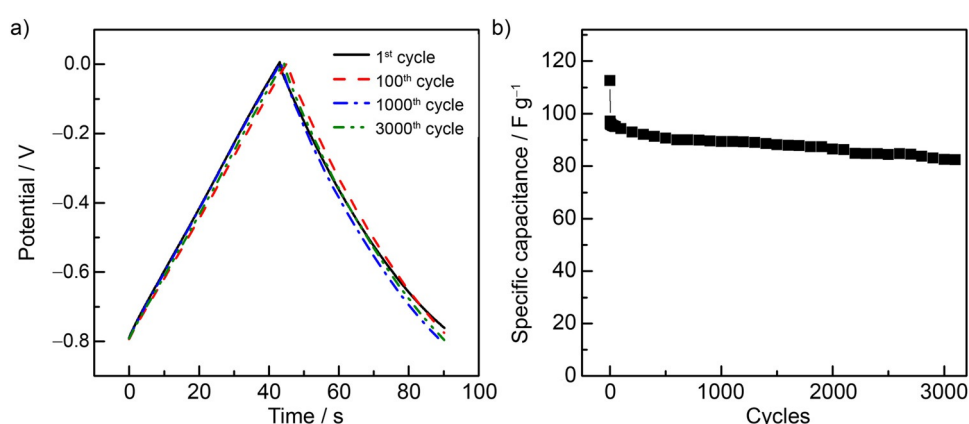


Figure 5. Galvanostatic charge/discharge (GCD) analysis of FP carbonised at 1500 °C. a) representative GCD curves of the 1st, 100th, 1000th, and 3000th cycle in 5 M aqueous KCl solution at a current density of 1 A g⁻¹; b) plot of specific capacitance against cycle number.

(117.21 F g⁻¹), which is more than triple that associated with samples carbonised at 1300 °C or 1700 °C. This value is very competitive to other carbon materials, such as carbon nanotubes (50 – 100 F g⁻¹),^[12] graphene (100 – 205 F g⁻¹)^[13] and activated carbon (28 – 100 F g⁻¹).^[14] The dramatic drop in capacitance at 1700 °C is likely because the high carbonisation temperature leads to the closure of micropores and small capillaries within the materials, resulting in a lower surface area. This phenomenon has been widely observed and reported.^[10]

The long-term cycle stability of the FP carbonised at 1500 °C was evaluated by GCD at a current density of 1 A g⁻¹ for 3000 cycles. Representative GCD curves of the 1st, 100th, 1000th, and 3000th cycles are shown in Figure 5a. Sample performance did not change significantly during continuous GCD cycling. The specific capacitance as a function of the cycle number is plotted in Figure 5b. A quick drop of the capacitance within the first 10 cycles was observed. However, the value was maintained above 95 F g⁻¹ thereafter, and 87% remained after 3000 cycles. These results show carbonised FP to have good electrochemical stability.

In summary, pure FP made from cellulose was successfully converted to a conductive carbon material by carbonising at

different temperatures from 600 to 1700 °C. After carbonisation, the primary microfibre structure was retained, with enhanced conductivity when carbonised at temperatures between 600 and 1500 °C. Within this range, conductivity was enhanced significantly with increasing carbonisation temperature. Surface characterisation shows this material to be contaminant-free, containing only carbon and a small number of oxygen moieties. FP carbonised at 1500 °C exhibited outstanding electrochemical performance as a supercapacitor.

The capacitance was obtained as high as 115 F g⁻¹, with more than 87% retained after 3000 charge–discharge cycles. This result is very competitive to other carbon materials like carbon nanotube, graphene, carbon aerogels and activated carbons.^[12,13,15] This work demonstrates that carbonised FP without the addition of additives can be a promising alternative carbon material for supercapacitor applications. FP has the advantage of being a pure, standardised material, which is more eco-friendly and simple to manufacture than noncarbon electrodes. This material can be further modified, such as surface modification by introducing metal/metal oxide, to develop hybrid systems in order to enhance the supercapacitance. On the other hand, this study identifies that a considerable amount of energy is still required to obtain the best electrochemical performance for cellulose-derived electrodes, and this remains a challenge.

Experimental Section

The FP was heated at 600 °C for 30 min under N₂ in order to fully remove the H₂O and decompose cellulose, followed by carbonisation at 1000 , 1300 , 1500 and 1700 °C for 30 min with a temperature ramp of 5 °C min⁻¹ (for an image of the carbonised FP, see Sup-

porting Information). Scanning electron microscope (S-4700, Hitachi, Japan), atomic force microscope (XE-100, Parksystems, Korea), and an X-ray photoelectron spectroscopy (XPS) using an Al K α source (1486.6 eV) were used to characterise the morphology, conductivity, and chemical composition of the FP samples. XPS peak position was calibrated to the adventitious C 1s peak at 285.0 eV.

Electrochemical measurements were performed at room temperature (20 \pm 2 $^{\circ}$ C) with μ -AUTOLAB III potentiostat (Eco-Chemie, Netherlands), running GPES software (version 4.9). A Pt wire served as a counter electrode and an Ag/AgCl electrode as the reference. The carbonised FP was cut into small square piece of 0.7 cm diameter, and directly used as working electrode with a titanium plate as the current collector. The capacitance was calculated by cyclic voltammetry and galvanostatic charge/discharge methods in A.C.S. reagent grade 5 M aqueous KCl solution (Sigma-Aldrich). All solutions were prepared with Milli-Q water (> 18 M Ω cm at 25 $^{\circ}$ C).

The specific capacitance values calculated from the CV results are based on Equation (1), where C_v is the specific capacitance of an individual sample, $\int_{E_1}^{E_2} i(E)dE$ is the total voltammetric charge obtained by integration of positive and negative sweep, E_1 and E_2 are the potential limits, m is the mass, and v is the scan rate.

$$C_v = \int_{E_1}^{E_2} i(E)dE / 2(E_2 - E_1)mv \quad (1)$$

The specific capacitance values calculated from the GCD results are based on Equation (2), where the I is discharge current, Δt is the discharging time, ΔV is the potential drop during the discharge process in the range of V_{\max} and $1/2 V_{\max}$, and m is the mass for the electrode materials. A scan rate of 5 mVs $^{-1}$ was used for GCD measurements used to calculate the specific capacitance.

$$C_m = \frac{C}{m} = \frac{I \times \Delta t}{\Delta V \times m} \quad (2)$$

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