A New High: Cannabis as a budding source of carbon-based materials for electrochemical power sources

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Declaration of competing interest

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Abstract

Cannabis sativa L., a low-cost, fast-growing herbaceous plant, is seeing a resurgence in widespread cultivation as a result of new policies and product drive. Its biodegradable and environmentally-benign nature coupled with its high specific surface area and three-dimensional hierarchal structure make it an excellent candidate for use as a biomass-derived carbon material for electrochemical power sources. It is proposed that this 'wonder-crop' could have an important role in the energy transition by providing high-functioning carbon-based materials for electrochemistry. In this paper, all instances of C. sativa usage in batteries, fuel cells and supercapacitors are discussed with a focus on highlighting the high capacity, rate capability, capacitance, current density and half-wave potential that can be achieved with its utilisation in the field.

Graphical abstract
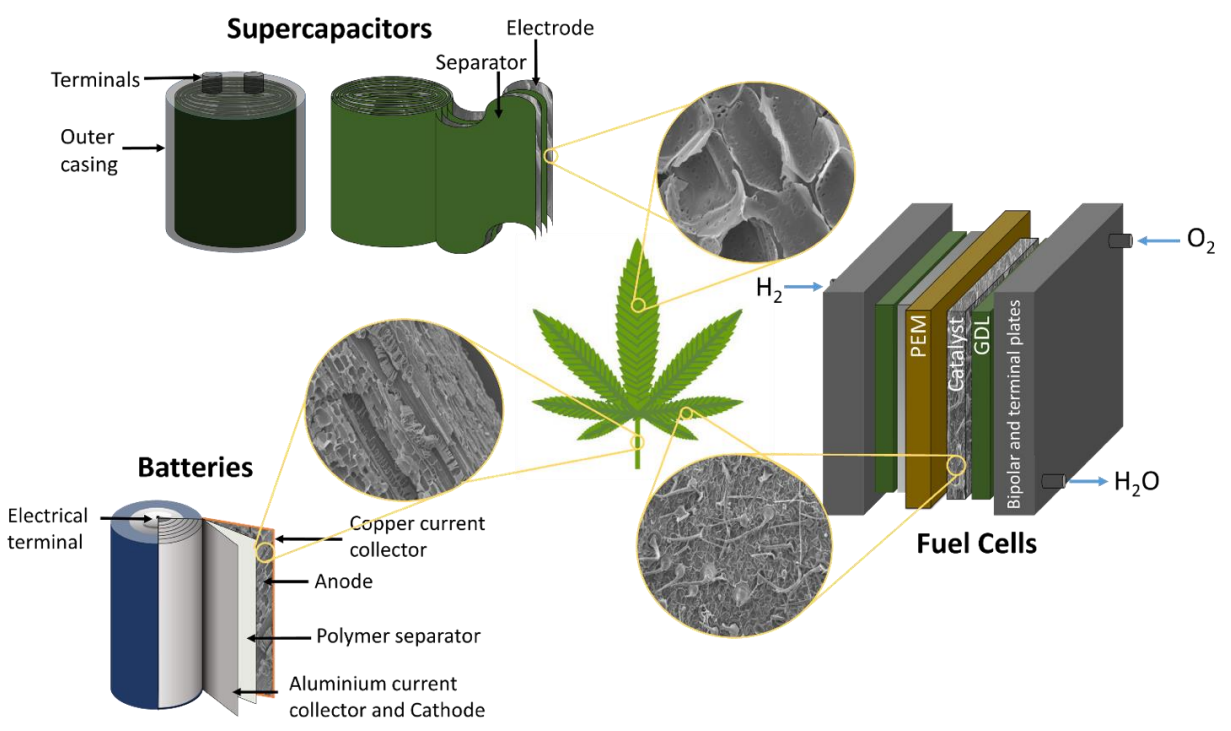
1.1 Introduction

Cultivated for millennia and one of the oldest domesticated plants in the world, Cannabis sativa L. (C. sativa) is an annual crop known for its sustainability and high yield [1,2]. With wide-ranging applications from food to fuel, the multipurpose plant was once (1938) hailed 'the billion-dollar crop of the era'[2], before a combination of reasons (including, but not limited to, concerns regarding its psychoactivity and recreational use) saw its cultivation cease for many decades in most Western countries [1]. However, it has now once again become the focal point of numerous research projects and industrial enterprises [3], with its carbon-negative [4], low-cost and biodegradable properties making it particularly attractive in the current climate crisis [5,6]. Furthermore, unlike traditional energy crops, C. sativa can be produced on marginal lands, meaning its production does not need to compete for high quality land needed for food and animal feeds [7]. Many believe the renewed interest in cannabis, together with the emerging global market of cannabis-based products, will help the crop once again become a leading sustainable agricultural feedstock.

A dioicous plant of the Cannabaceae family, C. sativa produces more than 750 natural compounds of different chemical classes. This includes 50 cannabinoids, 50 hydrocarbons, 34 sugars and 27 nitrogenous compounds [2]. Despite well-documented components, the taxonomic classification of cannabis has been considered difficult due to its genetic variability and ability to easily crossbreed [8]. **Error! Reference source not found.** shows the three main routes to classification: the first broadly differentiates between 'drug-type' and 'fibre-type' profiles, where the drug-type (with high levels of psychoactive tetrahydrocannabinol, THC) is used for medicinal and recreational purposes and the 'fibre-type' (also known as hemp or industrial hemp)is used for textiles and food. The second classification is through species and the third, identifies C. sativa as the only species and assumes all other variations are subspecies (chemotypes) of this. It is also important to note that 'industrial hemp' (C. sativa) is different to Manila hemp and Sisal hemp.

It is estimated that the global market for C. sativa consists of more than 25,000 products [9]. This is in part due to the diversified range of biomass acquirable from the crop, including hurds (i.e. coarse fibres and other woody components), fibres and seeds [10]. Whilst some uses of C. sativa are well established - specifically in the textiles and construction industries - more innovative applications are also gaining traction. Of these, there is a strong case for C. sativa's suitability as a low-cost and effective natural biomass precursor for electrochemical power sources, providing a much-needed alternative to traditional compounds that have complex synthetic processes or require by-product and waste management [11,12].

With C. sativa (as with other natural products), the conversion to biomass-derived carbon is accomplished through thermal carbonisation and activation that yields three-dimensional hierarchical structures with great potential for high conductivity, surface area and porosity [13,14,15]. With further research and development, this electrochemically and environmentally viable material has the capability to become an industry standard for fuel cells, batteries and supercapacitors. This review will discuss the work already accomplished in this field and make the case for why it is important to advance this research and cement C. sativa's position as the ideal precursor for carbon materials in electrochemistry.
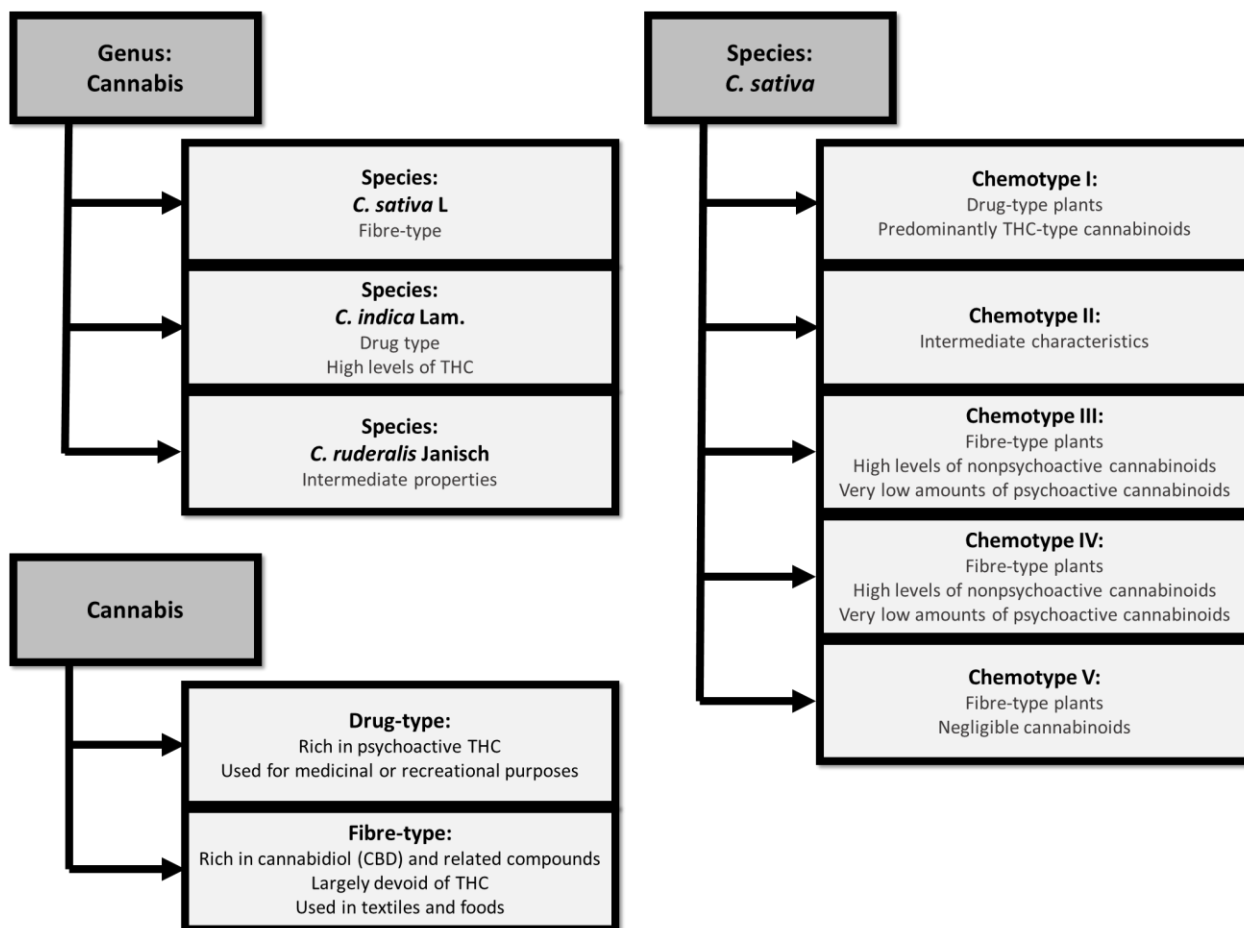
Figure 1 Cannabis classification routes based either on species, chemotype or THC profile.
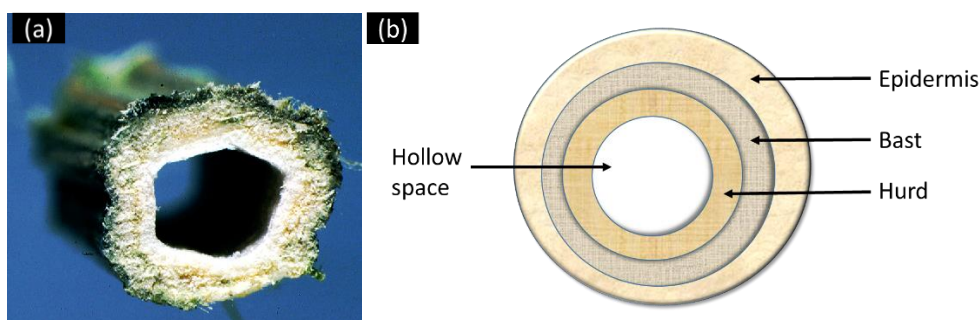
1.2 C. Sativa for electrochemistry

Figure 2 (a) Cross section of C. sativa stem [16] *(b) Schematic of C. sativa hemp*

Supercapacitors, batteries and fuel cells are critical enabling technologies for the overhaul of the current energy system. As the demand for these energy storage and conversion devices increases, so does the need to produce sustainable, low-cost and high-performing components for them. Of the various parts needed, the electrodes in these devices are vital in determining electrochemical performance (e.g. capacity, cycleability, durability), thus the constituent materials need to have certain properties such as high surface area and electrical conductivity [17]. To achieve this, a form of advanced carbon (porous/activated carbon (AC), carbon nanofibers (CNFs), graphite/graphene-like carbon etc.) is often employed in the electrodes of electrochemical devices either as an additive, a

support material or on its own. However, traditionally, this carbon is synthesised via energy/time-consuming processes involving the incomplete combustion of heavy petroleum products or coal [18]. An alternate, more environmentally friendly way to produce this is through utilising biomass precursors [19], of which C. sativa is a promising option.

Various components of the above-ground, harvestable C. sativa plant biomass can be utilised as a carbon source; including the bast (short inner stem fibres), hurd (long outer stem fibres) and leaves (Figure 2). Depending on application, and especially for electrochemistry, the materials are processed to present morphologies of high specific surface area such as AC, AC monoliths, AC fibres and interconnected nanosheets [20]. To achieve these morphologies, the C. sativa material is usually subject to carbonisation and activation procedures. The important parameters for this are the activating agent, heating ramp rate, activating agent:carbon material ratio and activation temperature – all of which influence the final product in terms of internal pore structure, specific surface area and surface functional groups [21]. This general processing technique was first used on C. sativa feedstock in 2008 by Rosas et al. for the production of AC monoliths via the chemical activation of the hurd with H_3PO_4 [22] and then again in 2009 by the same group but this time using the fibres [23]. Their results showed that the C. sativa derived AC had a high BET surface area of 1415 m^2 g^{-1} with only rice-straw derived AC demonstrating a greater BET surface area [24]. Other than H_3PO_4, KOH [25,26,27], $ZnCl_2$ [28,29,30] and steam [31] have all been used as activating agents with activation temperatures ranging from 400-950 °C. Figure 3 shows some of the synthesis routes for C. sativa-derived carbon materials as reported in literature with the resultant high surface area morphologies.

The subsequent sections will look at the specific literature for each electrochemical device

(a)

C. sativa	C. sativa fibres cut to the length of a few centimetres	Short fibres carbonised at 700 and 1000 °C under N_2 flow	Carbonised samples activated with KOH by mixing with KOH pellets and heating under N_2

(b)

C. sativa stems isolated, cut into pieces < 1.5 mm, carbonised and then activated using steam	Honeycomb 3D macroporous structure produced containing 5-60 µm sized interconnected macropores	Structure deposited with electroactive material MnO_2 (< 3 µm on inner and outer surface)

(c)

Peeled C. sativa stems washed, dried and pulverised	Powder heated to 300 °C for 3h under Ar, ground with $ZnCl_2$ and heated to 700 °C for 3h	Sample acid leached, washed with deionised water and dried

TEM patterns of C. sativa derived AC with (a) and without (b) the addition of $ZnCl_2$. AC with $ZnCl_2$ shows more obvious pores and thus more active sites and hence specific activity for the battery application
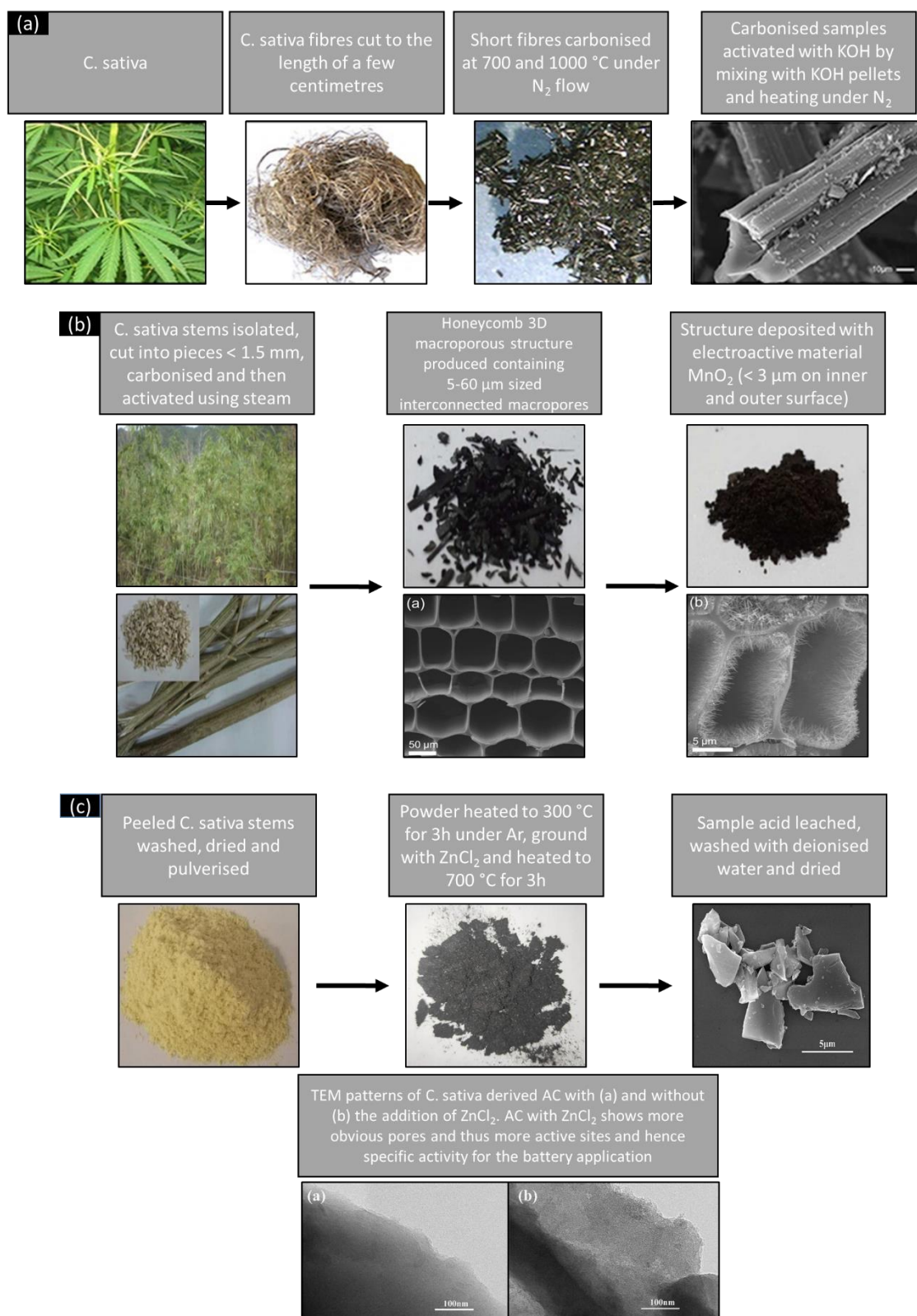
Figure 3 Various synthesis routes for the production of C. sativa-derived carbon materials (a) Production of activated C. sativa fibres by carbonisation in inert atmosphere followed by activation with potassium hydroxide. The final material had a relatively high specific surface area (up to 2192 m^2 g^{-1}) and a predominantly microporous structure [25] (b) Vertical MnO_2 wires were deposited on the surface of C. sativa derived AC via a one-step hydrothermal process. The final hierarchical porous structure had a high rate capability due to its open-pore system [31] (c) Production of C. sativa-derived nanoporous

carbon for use as anodes in lithium-ion batteries. The synthesis route involved low temperature carbonisation followed by high temperature activation with ZnCl₂. The final product showed a mainly microporous structure with excellent reversible capacity of 495 mAh g⁻¹ [29]
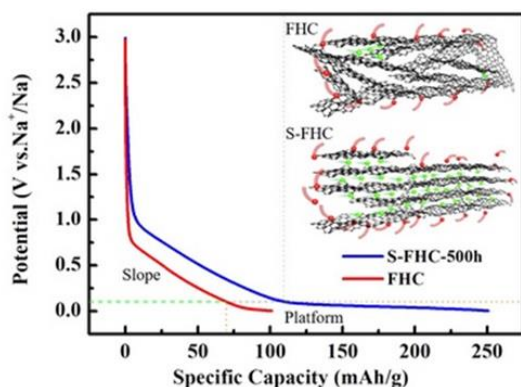
1.3 Batteries

Figure 4 Discharge curves of a free-standing hard carbon, FHC (synthesised from carbonisation of C.sativa), and its structure-reconstructed form, S-FHC (after high current cycling of FHC) against Na metal in a half-cell. Insets show the rearrangement of FHC to a more ordered structure in S-FHC, with larger capacity for Na⁺ ions [35]

Due to the ever-increasing demand for rechargeable batteries in many applications, from portable electronic devices to electric vehicles, finding more sustainable and cheaper electrode materials is imperative. At present, the industry standard for rechargeable lithium-ion battery anodes is graphite, which often requires extreme processing conditions. Research is therefore being focused on deriving graphite and other commercially important carbonaceous materials from naturally available biomass, such as C. sativa, using milder processing methods [32]. Electrode materials must also possess certain intrinsic properties to meet current demands of higher capacity, faster charge, and extended cycle life. In comparison to graphite, C.sativa has a more porous structure, and may therefore provide more storage sites for lithium ions [33]. Additionally, C. sativa products often have a larger interlayer spacing than that of graphite which may allow for faster transport of ions within the electrode, resulting in increased power density, and therefore faster charging [34]. Figure 4 shows an amorphous structure of C. sativa after carbonisation and a more ordered structure after electrochemically cycling at high currents [35]. Table 1 summarises the electrochemical performance of C. sativa-based materials in various battery chemistries.

Biomass materials are also of great interest due to their structural versatilities and various functional groups that can be exploited to improve performance for their desired applications [7],[36]. Wang *et al*. researched the effect of nitrogen and oxygen functional groups on C. sativa-derived carbon anodes for sodium-ion batteries [34]. The C. sativa bast fibre was activated with potassium hydroxide to produce "carbon nanosheets" which were then treated with urea under hydrothermal conditions to incorporate nitrogen and oxygen onto the surface. However, the nanosheet production was only supported by transmission electron microscopy (TEM) which included areas of both transparent sheets and opaque areas, indicating bulk material. The material had a very high BET surface area (2190 m² g⁻¹) which was greatly reduced by functionalisation (840 m² g⁻¹). It could be argued that the drastic change in surface area derived using BET method may not be the true reduction of surface area, but more likely a consequence of the change in surface adsorption energy of the gas used. Regardless, both forms displayed high capacity, excellent rate capability and had a long cycle life with a good

performance of 162/173 mAh g^{-1} at 1 A g^{-1} after 2000 cycles (50-60% capacity retention). It is thought the functionalisation led to chemisorption of sodium ions, allowing for extra capacity [34].

Cao's group also synthesised and tested a free-standing, C. sativa-based electrode for sodium-ion batteries. Natural C. sativa haulm was carbonised, sliced and then directly used as an anode in a sodium ion half-cell. The process eliminated the use of conductive additives, binders, and current collectors, which increase the cost and weight of a battery, without adding to its capacity. The best electrochemical performance was observed when the electrode was initially cycled at a high current rate of 1.8 A g^{-1}. An increase in the d-spacing was observed using ex-situ X-ray diffraction (XRD), while ex-situ Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that many defects were introduced after the initial high current cycling. The material exhibited a superior electrochemical performance of ~250 mAh g^{-1} compared to one that did not undergo initial high current cycling (~100 mAh g^{-1}). The authors attributed the higher capacity to the formation of a "reconstructed" material that included more storage sites, which was logically supported by their ex-situ characterisation as illustrated in Figure 4 [35].

Lithium-sulfur batteries have much higher theoretical specific capacities and energy densities than lithium-ion batteries, which make them a promising alternative for future applications [37]. However, currently, the commercialisation of lithium-sulfur batteries is hindered by the lack of suitable sulfur hosts for the cathode. Raghunandanan *et al*. synthesised C. sativa-derived carbon and MnO$_2$ composites for lithium-sulfur batteries. By mixing the sulfur and the KOH-activated C. sativa carbon, the conductivity of sulfur was improved whilst the MnO$_2$ absorbed the undesirable side products such as polysulfides that do not contribute to the capacity of the cell. It was suggested that the large surface area of their KOH-activated C. sativa (746 m^2 g^{-1}) allowed for easy absorption of many MnO$_2$ nanoparticles. The composite had a high capacity of 926 mAh g^{-1} but further work is required in improving the cycle life [38].

Um *et al*. were the first to employ C. sativa stem-derived carbon as an anode material for lithium-ion batteries. Unlike the papers discussed thus far, steam was used as the activating agent developing a partially graphitic carbon. The C. sativa is rich in cellulose and hemicellulose which provide its fibrous structure, and its many oxygen-containing functional groups that react with steam to form gases (H$_2$O, CO and CO$_2$) while introducing micropores. The graphitization of the carbon was then further enhanced by ball-milling which was verified by the sharper and narrower nature of the (002) and (100) reflections in the diffraction patterns and further confirmed by the ratio of intensities of the D (defect) and G (graphite) peaks in Raman spectroscopy. This was reflected in the reversible capacities obtained for each sample: with the partially graphitic carbon displaying a capacity of 190 mAh g^{-1} at a rate of 300 mA g^{-1} after 100 cycles; and the ball-milled graphitic carbon giving an increased capacity of 300 mAh g^{-1} under the same cycling conditions [33].

More recently, Guan *et al*. studied the use of C. sativa-based materials in lithium ion battery conditions, due to their 'sheet-like structures and slit-like interspace' which should enhance lithium ion intercalation. C. sativa was activated with ZnCl$_2$ at a range of temperatures (500-800 °C). The material synthesised at 600 °C gave the highest capacity in a lithium-ion half-cell of ~500 mAh g^{-1} at a rate of 74 mA g^{-1} for 100 cycles. The larger pore sizes observed in TEM and a larger BET surface area of the activated C. sativa-based carbon (compared with the unactivated material) were suggested as the origins of the high capacity and excellent stability. However, the unactivated starting material had better rate capability with higher capacities at 0.37, 0.74 and 1.86 A g^{-1} rates [29]. The same group

later treated their activated C. sativa-based materials in a cryogenic process, at -185 °C. In this case, the material activated at 500 °C showed the best electrochemical performance of ~750 mAh g^{-1} at a rate of 74 mA g^{-1} for 100 cycles. This superior capacity was likely a consequence of the introduction of larger pores during cryogenic treatment. Nitrogen adsorption/desorption experiments were used to confirm this theory where pore sizes of 3.55 nm and 2.65 nm were found for the cryogenic-treated material and untreated material, respectively [39].

In 2020, Cao's group synthesised another free-standing electrode, and this time tested its performance in a lithium-ion battery. In this study, products were collected from a hydrothermal reaction of carbonised hemp rods and Co_3O_4 between 8-18 h. The Co_3O_4 particles formed nanoneedles (8 h), nanowires (10 hrs), nanoneedles (12 h), microparticles (16 h), and finally, the carbonised C. sativa was covered with a 2 µm layer of Co_3O_4 (18 h), characterised by SEM and XRD. It was suggested that the C. sativa's hollow channel structure should enable easy access for the electrolyte. EIS revealed that the diffusion resistance was the smallest for the nanoneedle material, suggesting the highest ionic conductivity. This finding was corroborated by its electrochemical performance, since the nanoneedles gave the most stable and highest capacity during cycling, of ~450 mAh g^{-1} at a rate of 55 mA g^{-1} for 50 cycles [40].The potassium-ion battery is another promising area for research since potassium is more abundant than lithium in the earth's crust, leading to a more economically viable option [41]. However, the large ionic radius of K$^+$ ions often lead to slower diffusion within the battery. Cao's group investigated a biomass carbon from discarded C. sativa rod cores from a textile factory in potassium ion battery conditions. Phosphine gas, formed by the decomposition of sodium hypophosphite at 230 °C, was used to dope this material with red phosphorus. Raman, TEM and XPS characterisation methods confirmed the higher amount of oxygen in the doped material compared to that of the undoped, likely due to the introduction of phosphorus. The doped material gave a capacity of ~450 mAh g^{-1} at a rate of 40 mA g^{-1} for 50 cycles, which was about three times higher than the undoped material. It was suggested that the defects produced by the oxygen-containing functional groups aided to form a stable solid electrolyte interface (SEI) in the initial cycles and no further irreversible reactions took place. The authors detail that it is the strong P-O bonds that allow a strong SEI to form, yet do not mention any other role of the phosphorus. Most recently, the same group synthesised sulfur-doped carbonised C. sativa stalk and tested its capability in a high-temperature potassium-ion battery, at 60 °C. In its charge-discharge curve, the plateaus were more obvious for the high temperature conditions, compared to that of the cell at 25 °C. An increase in the ability of sulfur to adsorb K$^+$ ions was suggested for better performance at 60 °C, which was confirmed by the higher ion transmission rate and lower solution resistance found in EIS characterisation. This chemistry afforded a competitive practical capacity of ~450 mA h g^{-1} at a rate of 40 mA g^{-1} for 175 cycles [30].

Considering the various types of C. sativa-based materials discussed, it can be concluded that C. sativa is a versatile material that can be modified for a range of battery chemistries. However, these papers fail to explain the origins of this versatility. Most often, the articles state the use of C. sativa, yet do not specify how it is grown, which part is used or its chemotype, which can vary in morphology and chemistries. To this end, researchers should provide more detailed characterisations on their C-sativa starting materials. Surprisingly, C. sativa-based electrodes can not only match the practical capacity of the current, commercial graphite anode (~400 mA h g^{-1}), but often exceeds its electrochemical performance. Moreover, compared to synthesis requirements, C. sativa provides a promising route for obtaining affordable, sustainably-sourced carbon for electrodes in energy storage devices.

Material	Battery type*	Capacity (mA h g^{-1})	Rate (mA g^{-1})	Ref.
Co$_3$O$_4$ nanowires grown on carbonised C. sativa rods (free-standing)	Li-ion	450	55	[40]
Cryogenic treated, ZnCl$_2$-activated C. sativa carbon	Li-ion	750	74	[30]
ZnCl$_2$-activated C. sativa carbon	Li-ion	500	74	[28]
Ball-milled carbonised C. sativa	Li-ion	300	300	[33]
Sulfur-doped carbonised C. sativa	K-ion	450	200	[30]
	K-ion full cell	80	50	
Carbonised C. sativa doped with red phosphorus nanoparticles	K-ion	450	40	[28]
Free-standing carbonised C. sativa	Na-ion	250	37	[35]
N,O-doped carbon nanosheets	Na-ion	190	1000	[34]
Carbon Valley C. sativa fibres	Al-ion	80	50	[42]
MnO$_2$ doped, KOH-activated C. sativa carbon	Li-S	700	37	[38]

*All battery types are in half cell form, unless otherwise stated.
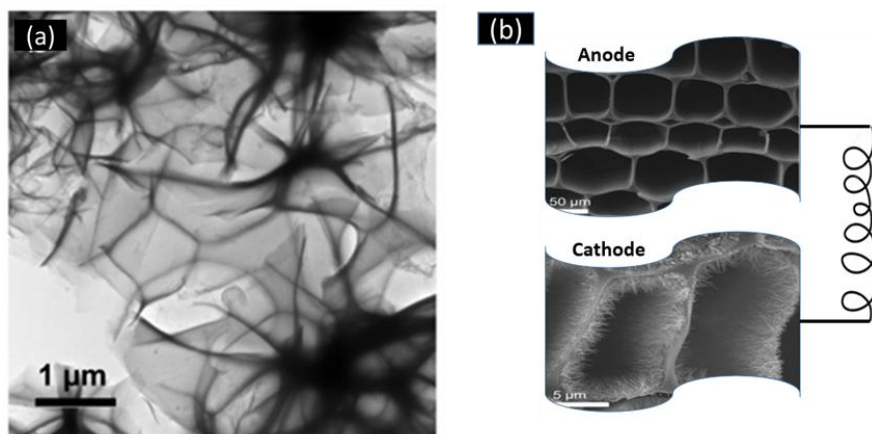
1.4 Supercapacitors

Figure 5 (a) TEM micrograph that highlights the structure of carbon nanosheets derived from hemp bast fibers, which consist of highly interconnected carbon nanosheets. Their macroporous voids are beneficial as they can serve as ion-buffering reservoirs during electrochemical testing [27] (b) Schematic of SEM images of the asymmetric supercapacitor constructed using HAC as the anode and MnO$_2$ nanowires anchored onto HAC as the cathode. Adapted from Ref [31]

Research into C. sativa as an alternative low cost and environmentally benign carbon precursor for supercapacitor applications is worthwhile as most of these devices are primarily based on, or somehow incorporate, activated carbon and carbon black materials in their electrodes. In addition, the performance characteristics of C. sativa-derived carbons give them the ability to be competitive in the current market.

Works by both Yang et al. and Wang et al. have explored the use of low-temperature hydrothermal carbonisation and subsequent KOH activation of a crude C. sativa stem to produce highly porous AC that have a large surface area of around ~3000 $m^2 g^{-1}$ [43,44]. The latter of the two reports stated that the C. sativa-derived AC (or hemp-derived activated carbon, HAC) achieved a respectable specific capacitance of 318 F g^{-1}, a value that is comparable to that of other commercial ACs which generally exist in the range of 100 to 400 F g^{-1} in aqueous electrolytes and around 120-150 F g^{-1} in organic or ionic liquid electrolytes [45].

Graphene materials have also been proven to have excellent electrochemical performance in supercapacitors that is often superior to that of AC. However, even the most economically produced graphene is nowhere near cost-competitive with petroleum- or biowaste-derived carbon. Wang et al. explored the synthesis of porous graphene-like carbon nanosheets from low-cost C. sativa and reported them to be 10 to 30 nm in thickness [27]. Their material performed with a good electrical conductivity of 211-226 S m^{-1} and a specific capacitance of 142 F g^{-1} at a current density of 100 A g^{-1} in an ionic liquid electrolyte. Moreover, the assembled electric double-layer capacitor (EDLC) reached a maximum energy density of 12 Wh kg^{-1}, a value higher than most commercially available supercapacitors. This work therefore highlights the benefits of using the complex multi-layered structure of the C. sativa based fiber as a precursor to enable the production of unique carbon materials with fundamentally different properties to other conventional biomass-derived activated carbons such as physical interconnectedness, high electrical conductivity, and a tuneable pore size distribution (Figure 5a).

As the energy density in EDLC devices is limited, much attention has been paid to pseudocapacitors which make use of materials such as metal oxides that can engage in Faradaic charge storage reactions. C. sativa-derived carbons used in conjunction with these metal oxides are beneficial as they serve as the conductive support matrix for the anchoring of redox-active materials in dual action electrodes that can simultaneously exploit both electrostatic and faradaic charge storage mechanisms [46]. These electrodes can provide 3D hierarchical architectures with high surface area, high electrical conductivity and efficient ion diffusion characteristics, all at a low cost.

Yang et al. explored the above by producing a uniform deposition of MnO_2 nanowires on the surface of AC derived from steam-activated C. sativa using a one-step hydrothermal approach to form a porous structure with conductive interconnected 3D networks that perform with a respectable specific capacitance of 340 F g^{-1} at a current of 1 A g^{-1} [31]. The asymmetric supercapacitor constructed using HAC as the anode and the synthesized MnO_2/HAC composite material as the cathode (Figure 5b) was able to store 33.3 Wh kg^{-1} with a power density of 14.8 kW kg^{-1}.

Similarly, Zhang et al. synthesised composites of homogeneously distributed RuO_2 particles anchored on the surface of the HAC through liquid phase co-precipitation and achieved an impressive performance of 652.79 F g^{-1} at 5 mV s^{-1} with a low equivalent series resistance of 0.653 Ohms and cyclability of 94.3% retention after 1000 cycles [47]. Other sources reporting on RuO_2/AC composite electrodes using commercial AC present specific capacitance values in the range of 60-290 F g^{-1} [48–50].

The success of the electrochemical results is attributed to the natural lignocellulosic fibers in C. sativa that can achieve a high rate capability due to the nature of the open-pore system that enables homogeneous electrical contact to accelerate the motion of electrons and pave the pathway for ion

mobility through the interior of the electrode [31,51,52]. These works prove that the C. sativa-derived activated carbons can serve as robust, active supports for metal oxides in pseudocapacitors to enhance the internal redox activity and confirm the success of a synergistic relationship between the two materials.

In a related study, Tiwari et al. combined $VO(OH)_2$ and HAC with the aim of widening the potential window of aqueous-based supercapacitors to 1.5 V from the typical 1.23 V restriction, the point at which water splitting reactions take place [53]. To rise above 1.23 V, a heterojunction was designed with electrode materials capable of accessing both the positive and negative potential windows. HAC was chosen as the negative electrode material because of its capability of reaching the lower potential range as well as its mesoporous structure that can facilitate the growth of $VO(OH)_2$ nanorods on its surface to form a charge storage path that is ideal for maximum utilization of the material.

The maximum specific capacitance calculated for the material in a symmetric set up at 2 A g^{-1} was an impressive 498.2 F g^{-1} with a high energy density of 149.31 Wh kg^{-1} at a power density of 1468.6 W kg^{-1}. This was an incredible improvement from the performance of the individual $VO(OH)_2$ particles that were only able to reach 56.8 F g^{-1} at 0.5 A g^{-1} on their own and the C. sativa derived activated carbon materials that separately produced a specific capacitance of 144.7 F g^{-1} at 1 A g^{-1}. The $VO(OH)_2$ phase was proved stable as it had a cycling performance of 96.1% retention after 10,000 cycles which is attributed to the strong adhesion of nanorods on the HAC sheets and serves as evidence of the structural stability of the material during repeated cycling. Other vanadium compounds combined with carbon nanotubes [54] or reduced graphene oxide [55] showed a significantly reduced performance of 58.02 and 70.3 F g^{-1}, respectively.

As summarised in Table 2, the studies reported thus far demonstrate the effectiveness of high performing supercapacitor devices with excellent electrochemical properties that are produced from C. sativa-derived materials. The unique properties of C. sativa fibre precursors make them ideally suited for application in both EDLCs and pseudocapacitors and are electrochemically competitive with other state-of-the-art graphene-based electrodes. It is shown to produce electrodes that have a high specific surface area, high rate capability and an excellent cyclability that are characteristically beneficial for supercapacitor applications and reinforce C. sativa derived carbons as promising candidates in electrochemical energy-storage applications.

Table 2 Electrochemical performances of C. sativa-based electrodes in supercapacitors

Material	Specific Capacitance (F g^{-1})	Current Density (A g^{-1})	Cycle Stability (% retention after # cycles)	Ref.
Activated carbon spheres	318	0.1	96% after 10,000 cycles	[44]
Carbon nanosheets	142	100	96% after 10,000 cycles	[27]
MnO_2 nanowires + HAC	340	1	98% after 3000 cycles	[31]
RuO_2/HAC	652.79	5 mV/s	94.3% after 1000 cycles	[47]
$VO(OH)_2$/HAC	498.2	2	96.1% after 10,000 cycles	[53]

1.5 Fuel Cells

Carbon materials, specifically carbon blacks, are often used as electrocatalyst supports in low temperature fuel cells due to their high accessible surface areas and electrical conductivity, ensuring conductivity between the electrocatalyst and the current collector [56]. To the best of our knowledge, there is only one paper describing the oxygen reduction reaction in proton exchange member fuel cells taking advantage of C. sativa in the electrocatalyst matrix. In this work, Zhang et al. used C. sativa together with an activator, a nitrogen source and cobalt precursor to produce a material with high pore volume (0.99 $cm^3 g^{-1}$) and high specific surface area (1251 $m^2 g^{-1}$) [57]. The final N-doped carbon material embedded with cobalt nanoparticles showed a high half-wave potential (0.826 V) as well as excellent stability and methanol tolerance. However, similar to the problems mentioned earlier with the lack of C. sativa identification and classification in research papers; here too, the C. sativa material was simply described as 'hemp powder' from the Shandog provice of China- making the work difficult to replicate. This is perhaps one of the reasons that despite these very promising results,, C. sativa has not been used otherwise in fuel cell applications, leaving a large gap for future seminal work.

1.6 C. sativa vs other biomass

Biomass is defined as the biological material derived from one of the following taxonomic groups: plant, bacteria, archaea, protists, animal or virus [58]. It has been used for a millennia in a variety of applications including energy, with dips in popularity coinciding with the rise in fossil fuel (19th century) and refined oil and gas usage (20th century) [59]. It is considering a sustainable and renewable source of carbon, with plant biomass accounting for an overall reserve of 450 gigtatons of carbon [60]. As the need for sustainable electrochemical devices increases, the last decade has seen increasing literature on biomass-derived carbons from hundreds of different agricultures as well as animal-based biomass (e.g. silkworm excrement [61], ant powder [62]) incorporated as electrodes in electrochemical devices. Many of these have been reported with very successful electrochemical performances in batteries, supercapacitors and fuel cells.

Walnut shells have been shown to be particularly successful biomass precursors in a range of battery chemistries; including as hard carbon in Na ion battery anodes (with 257 mAh g^{-1} reversible capacity) [63]; CNFs in high functioning lithium ion battery anodes (with initial charge capacity of 380 mA g^{-1}) [64] and AC in lithium-sulfur battery cathodes (with a reversible capacity of 910 mAh g^{-1} after 100 cycles) [65]. They have also been used extensively in supercapacitor research, with multiple papers reporting on the high specific capacitances possible by using walnut shell-derived porous carbons as electrodes [66] [67] [68] [69] [70] [71]. Whilst this research is very promising, there lies a problem with the annual global production of walnut shells being too little to supply the electrochemical industry [58]. This problem unfortunately relates to multiple biomass research areas that have shown very promising results but lack the production rates needed for commercialisation. In fact, other than electrochemical performance, the screening of biomass based on abundance (regional and global), cost, scalability, processability and processing yield is paramount. Disregarding these parameters contradicts the underlying principles of using biomass in the first place: renewable, abundant and low-cost alternatives to traditionally used materials.

C. sativa is regarded as one of the most sustainable plants due to its relatively low carbon footprint, easy agriculture- without need for specific climate or fertiliser [27], moderate water requirement [23], high yield and low pesticide requirements [20]. Furthermore, upon processing, the BET surface area of C. sativa derived carbons are often found to be such greater than 1000 $m^2 g^{-1}$ [43] [44] [22] [57], which is not the case for many other biomass-derived ACs [19]. These parameters make C. sativa the ideal choice for electrochemistry. However, it is worth noting the lack of direct comparison of different biomass precursors within the same system. In fact, of the C. sativa papers reviewed, only one group

compared performance against a different biomass: activated human hair against activated C. sativa fibres in a Al-ion battery [42]. They found that the activated human hair electrode exhibited a slightly higher capacity (90 mA h g^{-1} vs. 80 mA h g^{-1}, respectively, at a rate of 50 mA g^{-1}) and had better rate capability. Although this biomass showed marginally better electrochemical performance, its abundance and availability is much lower than C. sativa and therefore is a much less sustainable option. Thus, when choosing an appropriate biomass precrusor, multiple factors need to be considered to ensure the choice is a viable long term solution.

1.5 Future outlook

C. sativa is seeing a resurgence in significance as its usage in a wide array of applications increases, with its future as a feedstock in a circular economy becoming increasingly likely [24] [17]. Its ability to grow in marginal land coupled with its sustainable and environmentally-benign design makes it perfect for use in the current climate landscape. As demonstrated in this paper, significant inroads have already been made into proving its effectiveness as an excellent biomass precursor for electrochemical power sources; with its usage equalling high specific surface area, rate capability, capacity, cyclability and half-wave potential, depending on application.

There are some issues to overcome in this research direction to ensure its continued success. Among them is the ambiguity surrounding the formation mechanism during the carbonisation process from C. sativa to the final structure. This issue affects many biomass precursors with only a few papers attempting to correlate the components of the utilised biomass, to the changes during processing, to the subsequent properties of the derived carbon; with also very little data on the electrochemical performance under realistic conditions [58][72]. Thus, more robust cataloguing of changes is required to better understand the mechanistic chemistry, as well as long term testing in real world conditions. Furthermore, specific to C. sativa research, better classification is needed of the type and part of the plant material used to enable propagation of the research. As well as that, to achieve better comparison in literature, testing against standard commercial materials (in their specific testing conditions) is essential to standardise this field of research. This will help continue the momentum and exploration of this research direction that will help cement C. sativa's position as a 'wonder-crop' in the field of electrochemistry.

Acknowledgments

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The only paper to date using C. sativa for the oxygen reduction reaction in proton exchange member fuel cells, though it only describes C. sativa as 'hemp powder' which makes it difficult to replicate.