Recent Advances in Biochar Modification for Energy Storage in Supercapacitors: A Review

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Biochar, also known as black carbon, has been studied extensively for both agricultural and environmental benefits. Biochar has ability to improve the soil quality, to remove inorganic pollutant and to reduce CO_2 emission rate. All these qualities of biochar are based on its physical and chemical properties, such as macro and micro porosity, particle density, high surface area etc. The recent studies on biochar have been suggested that the developments in activation procedures and precursors improve its pore structure and surface properties. These improved characteristics have widened the application of biochar in energy storage devices (ESDs). Biochar as energy storage material is an important aspect to report that has not been reviewed well in recent past. This review elucidated the modification methods applied for biochar improvement and their significant applications in ESDs as supercapacitor (SCs). The brief explanations of biochar production process, modification methods that affect biochar performance, followed by potential applications in energy storage domain are also addressed.

Introduction

The continuous consumption of conventional sources of energy like fossil fuel (coal, oil, gases and radioactive ore) and growing human population has increased the demand of energy all over the world. Associated environmental impacts of declined natural energy resources lead to more efforts to decrease the dependence on these resources by introducing new ideas for renewable energy materials. Energy is crucial in the development of transportation, industrial, defense, medical and agricultural sectors of any developed and developing country. This rising demand in energy has led to the development of an ideal material that must be low cost, less polluted to ecosystem and meet the all-energy requirements at large scale. In this regard, biomass can work as future power-energy storage applications using green chemistry approaches for production of various bio-carbons [2,3]. Biomass is a naturally abundant renewable carbon resource that can replace fossil derived products; it has great potential for energy production [4]. The introduction of biomass and its derived products, can resolve various social and environmental energy issues [5,6]. The thermo chemical conversion of biomass produces biofuel, bio-oil, combustible gases and an important sustainable carbon material (biochar) at different temperature and heating conditions (**Fig. 1**). Biomass derived carbon materials are cost effective, biocompatible, less hazardous to living
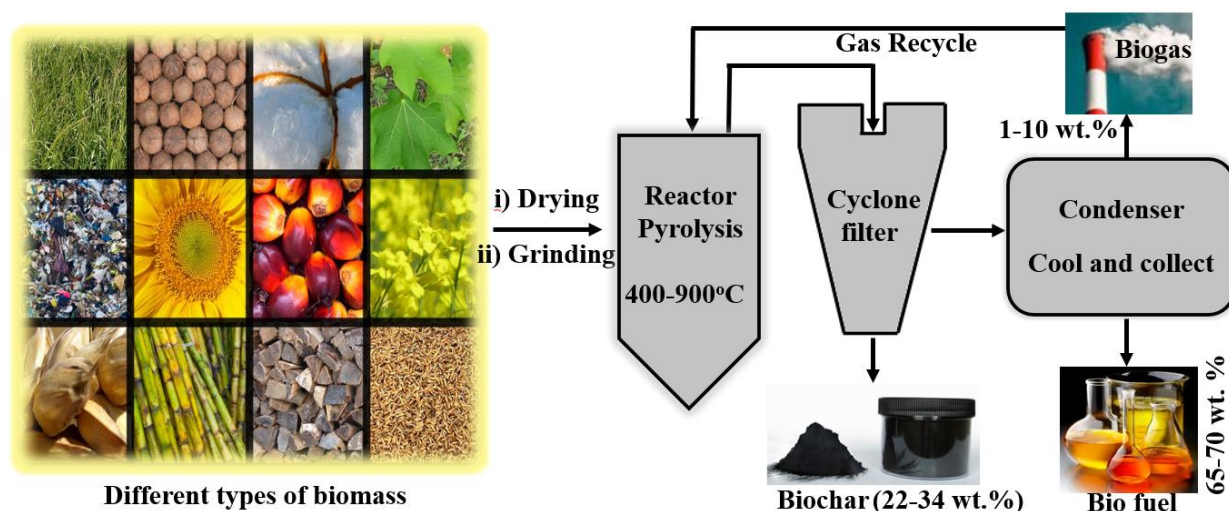

Fig. 1. Schematic diagram of biomass pyrolysis products.

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being and environmental friendly, as they are synthesized by natural precursors. As compared to other carbon sources (coal and other petrochemical products), biomass derived carbon materials are very effective energy carrier and also used to produce electricity due to its intrinsic properties like, low bulk density, high porosity and effective surface interactions with abundant functional groups [7-9]. Biomass have wide applications in various field, such as sorption, contamination, water purification, bio-catalysis, sensors, electro catalysts and energy storage in SCs [10-12]. Use of waste biomass as feedstock to produce cost effective carbon electrodes for SCs has become a common trend among the researchers.

Biochar, a biomass derived carbon is sustainable and green material as it is cost effective, environmental friendly, recyclable, renewable and show desirable physical-chemical properties for various applications [13,14]. Currently, biochar shows great potential applications to meet out the energy demands in industries and ESDs [15]. Use of biochar for soil nutrient retention has been originated over 2,500 years ago in the Brazilian Amazon. Wide range of biomass such as agricultural residues, algal biomass, forest residues, manures, activated sludge, energy crops, digestate etc. are used in the production of biochar [11,12]. Biochar is developed by thermochemical conversion of biomass under limited or oxygen free condition in specially designed furnace capturing all emissions at high temperature [16]. The chemical composition, physical and mechanical characteristics of biochar is controlled by the pyrolysis operating conditions and feedstock sources. In agriculture, biochar improves the quality of soil by holding the soil moisture and decreasing the nutrients decomposition rate. In the field of wastewater treatment, adsorption properties of biochar are utilized to remove the organic pollutants [17], heavy metals [18], nitrogen and phosphorus [19] present in contaminated water. Biochar is also considered as a potentially attractive controlled release nitrogen and phosphorus fertilizer due to its good adsorption capacity for nitrogen and phosphorus and enhanced water-retention ability [20].

Besides all these applications, biochar has attracted much attention in power generation and ESDs such as SCs [21,22]. The electrochemical performance of SCs are mainly dependent on the physical characteristics of electrode materials as electrodes are the main component of SCs. In addition, the cost of the electrode material along with its impacts on environment play a key role to design the SCs. The physical properties of biochar such as effective porosity (Meso and Micro both), excellent surface functionality and high percentage of carbon content are explored the biochar as promising electrode material for the next generation of SCs [23]. Therefore, morphology, porosity and surface chemistry are regulating parameters for biochar, that can either limit or widened its applications in ESDs. Utilization of low-cost biochar in SCs can be increased at a large scale if these regulating parameters were modified further. The reason behind this

is, modifications in physical characteristics of biochar cause numerous changes in its microstructure which is responsible for improved electron conductivity and excellent capacitive performance in biochar [48].

Recent studies on biochar have revealed that the improvement in physical properties of biochar does not only depend on the pyrolytic procedures, but also controlled by various chemical modification methods to maximize the effectiveness and performance of developed biochar for energy storage in SCs [24,25]. Keeping the all above points under consideration, this review attempts to emphasize the important modification methods to improve the physical characteristics i.e., morphology, porosity and surface functionality of biochar to show their large applications for energy storage in SCs. In addition, the presented text will be focused on the common production process of biochar in brief and highlights the recent potential advances in energy storage applications of biochar-based composites as SCs electrode materials.

Production of biochar

Biomass conversion in the biochar can be performed by three processes namely, gasification carbonization and pyrolysis. Biomass gasification is a partial oxidation process of biomass at temperatures varying from 800-900°C, that generate syngas and biochar as two main products [1]. In this process the yield of biochar is generally 5-10% of biomass, which is comparatively lower than biochar produced from pyrolysis. Pyrolysis technology is of interest from long time as it has lot of advantages based on process parameter optimization. Pyrolysis involves thermo-chemical conversion of biomass under partial (or complete) absence of oxygen and controlled temperature range from 300-900°C [16, 24]. Pyrolysis is not an independent process, it also involves both carbonization and gasification steps [1,2]. Pyrolysis process occurs at two levels: at first level gaseous product is obtained through dehydrogenation, dehydration, decarboxylation and at second level breakdown of large molecules take place [26]. In pyrolysis long carbon chains, organic groups and high-molecular-weight compounds present in biomass get break down and form gases, oils and solid charcoal [27]. Major product of biomass pyrolysis varies with temperature variation as it forms solid (biochar) at less than 450°C, gases (syngas) at greater than 800°C and liquid (biooil) at intermediate temperature [26]. Pyrolysis involves a variety of physical and chemical changes of biomass such as C/N, H/C and O/C ratio alterations, porosity modification and functionality of surface also get altered [28-31]. Depending on the process parameters (heating rate, heating temperature, residence time and biomass particle size), pyrolysis can be further classified into conventional pyrolysis (slow pyrolysis), fast pyrolysis, flash pyrolysis and intermediate pyrolysis [29]. In brief, slow pyrolysis is an ancient technique to convert biomass into biochar as a main product that takes several hours. In slow pyrolysis, heating rate of biomass varies from 0.6-6°C/min with

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Table 1. Biochar yield by different pyrolysis process.

Pyrolysis type	Temp. (K)	Residence time (s)	Heating rate (Ks^{-1})	Particle size (mm)	Product			Ref.
					biofuel	syn gas	biochar	
Slow	500-950	450-600	0.1-1	10-55	15-50	15-50	30-35	[33-35]
Fast	500-1250	2-10	15-250	<1	60-75	10-25	10-20	[36, 37]
Flash	1000-1350	<0.5	>1000	<0.1	60-75	10-15	10-15	[34, 38]

higher vapor residence time that produces more biochar as compared to fast pyrolysis (**Table 1**). On the other hand, in fast pyrolysis higher temperature with rapid heating rate is required for thermal cracking of biomass into biochar. Fast pyrolysis produces the biofuel as primary product due to less residence time to connect with solid phase [**32**]. Fast pyrolysis of biomass produces 65-70 % biofuel, 22-34% biochar and 1-10% syn gases (**Table 1**).

Modification of biochar for their wide applications in SCs

Different modification methods have been carried out in order to obtain biochar with superior electrochemical properties so that the applications of Biochar in SCs could be widened. Biochar is modified to create surface with improve and desired properties, through physical and chemical treatment of original biochar. Chemical analysis showed that the modified biomass show improved fuel qualities compared to the raw biomass, such as decreased volatile matter/(volatile matter + fixed carbon) ratio, increased carbon content and lower ash content [**5,27**].

Modification of biochar alters the specific surface area (SSA) and size of pores as well as their content in biochar which finally enhanced the adsorption capacity of biochar for polar or non-polar adsorbate and energy storage capacity as well [**39,51**]. Pourhosseini *et al*., [**40**] developed a biochar electrode material for energy storage via slow pyrolysis of Cladophora glomerata and modified this obtained biochar through an activation process with HNO$_3$ to enhanced its energy storage properties. It was found that HNO$_3$ increased dramatically the micro/macro porous contents in biochar due to which the activated biochar electrode demonstrated high specific capacitance, and excellent cycle stability. In addition, electrochemical studies reported two times more specific capacitance for activated biochar than that of raw biochar. In modification process activation time, type of activator, activation temperature and soaking time, also affect the properties of biochar. The biochar can be activated by different modification methods as discussed in following sections.

Acid treatment

Chemical oxidation or acid treatment of biochar surface is carried out to develop more mesopores, improve surface functionality and hydrophilic nature of biochar by increasing oxygen functional groups on its surface [**41**]. The mesoporous surface of electrodes is more capable to store the energy (electrical or thermal), due to their efficient capability to penetrate the electrolytes ions through it. Literatures reveal that to improve the electrochemical performance of electrodes in SCs, doping of oxygen and nitrogen in carbon materials is an appreciable effort because these both hetero atoms provide pseudo capacitance to that particular electrode material in which they are inserted. Ammoniate treatment and oxidation of biochar are the most common used methods to introduced nitrogen and oxygen heteroatoms into biochar, respectively [**42**]. Pyrolysis of nitrogen rich polymer is also an efficient way to develop nitrogen doped biochar based SCs. HNO$_3$, HCl, H$_2$SO$_4$, H$_2$O$_2$, H$_3$PO$_4$, etc. are commonly used reagent for acid treatment to provide multifunctional biochar [**43-45**]. Oxygen enriched C-S-C moieties are found to be useful for excellent electrochemical performance in carbon-based electrodes, as these moieties decrease the energy gap between valance band and fermi level. Moreover, under high positive potential range, C-S-C moieties prevent the further oxidation of carbon materials and boost up the stability of carbon materials [**46**]. In this regard, sulphonation of lignin was carried out in the presence of NaOH and Na$_2$SO$_3$ to incorporate oxygen enriched C-S-C moiety into lignin based biocarbon (LBB). The as prepared multi porous LBB performed excellent redox activities under in both acidic and alkaline electrolytes with 140 Fg^{-1} specific capacitance at 0.5 Ag^{-1} current density [**46**].

Alkali treatment

Alkali modification or chemical reduction method is deals with the surface activation of biochar with reducing agents, such as NaOH [**47**] and KOH [**48,49**]. Reducing agents are used to enhance the non-polar nature of biochar by reducing the functional groups on the surface of biochar, therefore it will be ease to alter the surface functionality of biochar as well as the energy storage capacity through alkali treatments. addition, the increased adsorption capacity of biochar has been observed after alkali treatment, SSA and porosity of biochar changed at large level [**50,51**]. Alkali modified biochar has a strong ability to filter heavy metals from aqueous solutions so it can serve as alternative adsorbent for heavy metals, in this context Zhuhong *et. al.,* [**47**] reported the significantly changes in the biochar's surface area, cation-exchange capacity and thermal stability after modification of biochar with NaOH. Moreover, in the mixture of Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} metal ions, modified biochar exhibited 2.6-5.8 times more adsorption capacities for Pb^{2+} and Cu^{2+}

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metal ions, than the pristine biochar. Not only adsorption capacity of biochar but electrochemical performance of biochar also depends on the porosity and SSA of biochar. In alkali treated biochar, redox reactions between biochar and alkali hydroxide (KOH and NaOH) increase the number of micropores with a decrease in mesopores due to which redox behavior of biochar is induced and consequently, efficiency of SCs. KOH and NaOH activated biochar when treated with $CaCO_3$, it dramatically inhibits the change in porosity during alkali treatment and some loss of capacitance and SSA in biochar has also been observed [**48**]. Dehkhoda *et. al.,* [**51**] showed the effect of KOH activation on both meso and micro porous nature of biochar and their individual impacts on capacitive behavior of biochar. It was observed KOH increase the content of micropores in biochar and therefore, capacitance (222-245 Fg^{-1}). On the other hand, increment in mesoporous content slightly decreased the total capacitance of biochar electrode material and reached to almost ideal capacitive behavior on further rise in mesopores.

Metal impregnation

In metal impregnation adsorption or doping of metal ions are take place onto the surface of biochar which increase the specific surface area to improve electrical conductivity and capacitance performance of biochar electrode materials for SCs. Kouchachvili *et. al.,* [**52**] developed a promising carbon electrode material Ag/BC for SCs by incorporation of silver into HNO_3 activated biochar. The silver content in biochar increased the electrochemical performance and electrical conductivity of biochar composite. In addition, Ag doped biochar coating displayed 494 Fg^{-1} more specific capacitance when compared with activated biochar coating (376 Fg^{-1}). Iron [**53**], magnesium [**54**], aluminum [**55**], zinc [**56**] are the most common used metal ions for doping of biochar to get biochar-based nanocomposite. Metal ion doping produce some graphitic nature in biochar that increase its applications in ESDs, especially in SCs. Yang *et. al.* [**57**] reported a novel carbon material obtained from bio-waste shaddock endothelium. KOH activation and Co^{2+} impregnation of WSE provided a highly ordered foam like porous structure with high level of heteroatom (nitrogen, oxygen and sulfur) doping in WSE showed excellent specific capacitance (550 Fg^{-1}). Moreover, a high degree of graphitization in WSE was introduced when treated with $Co(NO_3)_2.6H_2O$, which is responsible for high capacitive retention after 1×10^4 cycles. Pine cone biochar (PCB) was modified with KOH treatment followed by insertion of Molybdenum (Mo) metal by using aqueous solution of phosphomolybdic acid ($H_3PMo_{12}O_{40}^{3-}$). KOH activation of PCB resulted not only high SSA but also enlarge the size of micropores in the 1-2 nm range. The as prepared PCB-Mo electrode material was found to be cost effective with effective capacitance behavior of value 361 Fg^{-1} (gravimetric capacitance and 1.19 Fcm^{-2} (areal capacitance) [**58**].

Application of biochar for energy storage in SCs

SCs have attracted broad research interests for energy storage systems as it shows a series of advantages, such as long-life cycle, fast charge discharge rate, high capacitance (from 1 mF to >10,000 F), superior performance at low temperature (from -40ºC to 70ºC) and longevity (about 10 to 15 years). SCs have potential to compliment or replace the batteries as it has high power density over batteries. Energy storage capability of SCs make it a versatile candidate in transportation, solar cell, electric drives, uninterruptible power sources (UPS), LED flashlights, digital communication system etc. The electrochemical performance of SCs is affected by mesoporous and microporous nature of the electrode materials. Many researches focused on the development of advanced carbon materials for SCs with better surface structure, morphology and porosity. In this context, biochar has received much interest in energy storage due to its high surface functionality, porosity, surface area and more carbon content [**59**]. Efficiency of biochar as energy storage material is significantly affected by temperature variations like, wood and miscanthus biochar at 500°C has relatively low conductivity due to low crystalline nature at this temperature [**60**]. So, studies have begun to observed the energy storage performance of biochar and the effect of biochar structure as it plays a crucial role. Improved porosity of biochar or modified biochar enhances the performance of SCs and also employed as porous matrix to host active substrate for cathode. For example, Dehkhoda *et. al.,* [**61**] has been reported that the biochar, activated with KOH have predominantly porous structure which showed improved capacitance value between 182 and 240 Fg^{-1} due to its mesoporous structure and an increase in micro porosity improved the capacitive behavior (222 and 245 Fg^{-1}) by reducing electrode resistance. An oxygen plasma activation of biochar is reported by Gupta *et. al.,* [**62**]. This treatment increased the pore size and microstructure of biochar which enhanced the capacitance of biochar by 2.84 and 1.72 factor of untreated and conventional chemically active biochar respectively. Hydrothermal carbonization was found to be highly useful method to upgrade waste biomass and increase its electrical conductivity at temperatures ranging from 150 to 375°C and a residence time of 30 min. Generally, electrical conductivity of biochar is ignored as it is considered as solid fuel for combustion. Electrical conductivity of biochar is highly dependent on its carbon content. It is found that micro and macro structures of biochar also play key role to regulate the electrical conductivity of biochar. Therefore, carbon content from 86.8 to 93.7 wt% increased the bulk conductivity of a monolithic biochar by over six orders of magnitudes. **Fig. 2** explains, the highest skeletal conductivity (343.2 S/m) is found in a heat-treated sugar maple biochar with 96.2 wt% of carbon which is more than graphite conducting fluid (333.3 S/m). It is observed that compressive loading or pressure is also a key

parameter to determine the conductivity of monolithic biochar that define the elastic behavior for electrical conductivity of biochar [63]. Compression eliminates the void space in the internal structure of biochar through flattening of porosity and make better contact between carbon particles of biochar which results good conductivity. Therefore, compression increased the conductivity at beginning until first fracture introduced in monolithic biochar (**Fig. 3**).
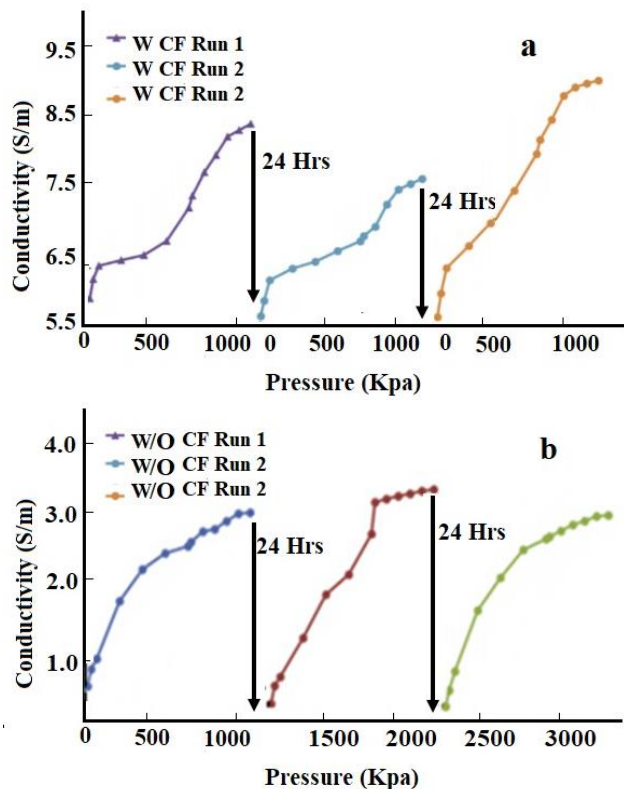

Fig. 2. Conductivity vs pressure analysis for sugar maple biochar with (a) without (b) graphite conducting fluid [63].
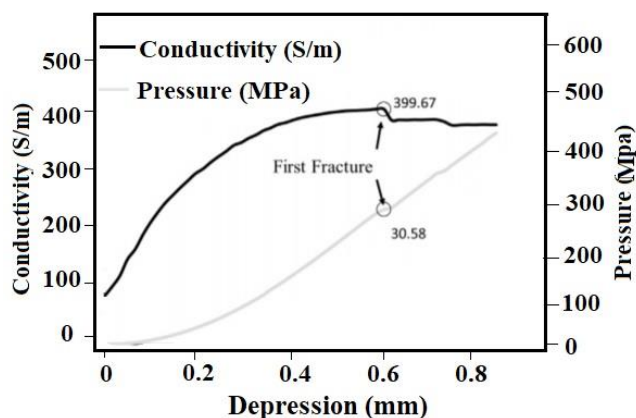

Fig. 3. Pressure effect on conductivity of sugar maple biochar [63].

More studies on applications of biochar-based composites for energy storage in recent years have been summarized in **Table 2**. Researches on biochar have been proved that biochar is well known for bioenergy production and climate change mitigation [106]. N-doped carbon derived from biomass by one-step carbonization activation method, display excellent specific capacitance ($330\ Fg^{-1}$) and may find future applications as energy storage materials [107].

Biochar/polyvinyl alcohol (PVA) composites, with biochar having 61.8 % carbon content, was able to showed similar conductive properties as one prepared with CNTs and graphene [108]. It was also reported that biochar/PVA composites act as a pressure sensor, giving another large potential application [109]. Biochar can also serve as a microbial electron donor and acceptor for nitrate reduction [110]. A wood derived biochar transfers an electron from acetate to nitrate with the help of Geobacter metallireducens (GS-15). Hence, microbially charged biochar can also work as electron storage material and electron storage capacity was found to be 0.85 and 0.87 $mmole^-/g$, based on acetate oxidation and nitrate reduction, respectively (**Fig. 4**).
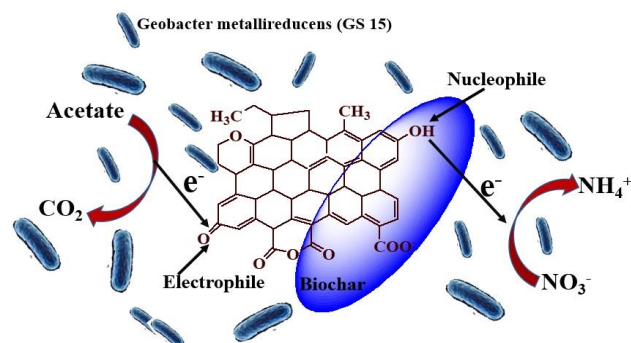

Fig. 4. Electron transfer mechanism of microbial charged biochar [110].

Biochar/metal oxide nanocomposites display good surface redox activity which can increase its pseudo capacitance properties. For example, MnO_2 dispersed evenly on the surface of wood derived biochar (WDB) *via* in situ redox reaction between biochar and $KMnO_4$. The WDB/MnO_2 nanocomposite worked as an eco-friendly supercapacitor with core shell structure and its electrochemical measurements revealed that WDB/MnO_2 composite exhibit typical rectangular-shape voltammetry responses at 0–0.8 V. This composite displayed a fast charge–discharge behavior with moderate specific capacitance of about 101 Fg^{-1} at a current density of 0.05 Ag^{-1} and a favourable cyclic stability with a capacitance retention of 85.0% after 10000 cycles also revealed [111].

Sugarcane bagasse carbon (SBC) with MnO_2 nanosphere worked as a good electrode material for SCs with high specific capacitance. Homogeneous dispersion of MnO_2 nanosphere on the surface of porous SBC by hydrothermal method, provided an electrochemically active SBC/MnO_2 nanocomposite. SBC/MnO_2 composite displayed much higher specific capacitance (747 Fg^{-1}) than MnO_2 nanosphere at 1 Ag^{-1} [112]. Silkworm excrement (SE) derived biochar (i.e., original-SE and pickling-SE) can also use for SC electrode material at high

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Table 2. Applications of biochar as energy storage material in SCs.

Composite material	Binder	Electrolyte	Capacitance	Ref.
BC/NiO	Polyvinylidene fluoride	NaOH (1M)	10.66 Fg^{-1}	[64]
Bimetallic Co/Mn-MoFs @Rice Husks	-	KCl (2 M)	32.8 Fg^{-1}	[65]
MnO_2/Wood derived BC	-	Na_2SO_4 (1M)	101 Fg^{-1}	[66]
MoS_2/corncob-derived activated carbon	Acetylene black	Na_2SO_4 (1M)	38.3 Fg^{-1}	[67]
BC/NiO	-	KOH (1M)	1058 Fg^{-1}	[68]
Polyoxometalate/pine cone BC	PVDF	H_2SO_4 (1M)	1.19 Fcm^{-2}	[69]
S doped SnO_2/Rice husk BC	Polytetrafluoroethylene (PTFE)+ AB	KOH (6M)	215 Fg^{-1}	[70]
N enriched Lignosulfonate BC	PTFE+AB	H_2SO_4 (1M)	950 Fcm^{-3}	[71]
Reduced graphene oxide modified BC	-	NaCl (0.05M)	167 Fg^{-1}	[72]
KOH activated mung bean husks BC	PTFE+ AB	Na_2SO_4 (1M)	287 Fg^{-1}	[73]
Cotinus coggygria flowers BC	-	H_2SO_4 (1M)	413.5 Fg^{-1}	[74]
KOH activated biochar based porous carbon nanofibers	-	NaOH (6M)	108 Fg^{-1}	[75]
MnO_2\ Switchgrass BC	PVDF+Carbon black	KOH (1M)	110 Fg^{-1}	[76]
NiO/MnO_2/pomelo peel, NiO/MnO_2/buckwheat hull	PTFE+AB	KOH (6M)	-	[77]
CeO_2/yellow bean sprout BC	PVDF+AB	KOH (6M)	752 Fg^{-1}	[78]
Porous wood carbon/MnO_2/graphene quantum dots	-	Na_2SO_4 (1M)	2712 $mFcm^{-2}$	[79]
KOH activated hierarchical porous biomass carbon	Nafion+AB	H_2SO_4 (1M) KOH (6M)	345 Fg^{-1} 330 Fg^{-1}	[80]
KOH activated longan shell as activated carbon	PTFE	KOH (6M)	210 Fg^{-1}	[81]
Biomass derived nanocellulose fibers/MnOx	PVDF+AB	Na_2SO_4 (1M)	269.7 Fg^{-1}	[82]
Porous hierarchical activated carbons	PVDF+AB	KOH (6M)	225 Fg^{-1}	[83]
KOH activated walnut Shell-derived hierarchical porous carbon	-	KOH (6M)	262.74 Fg^{-1}	[84]
N-doped hierarchical porous bio-carbon from cherry stones	-	KOH (6M)	225.1 Fg^{-1}	[85]
KOH activated waste litchi shell as porous carbon nanosheets/particle composites	PTFE+AB	KOH (6M)	222.0 Fg^{-1}	[86]
Ascophyllum nodosum KOH activated biocarbon	PVDF	KOH (1M)	207.3 Fg^{-1}	[87]
N/S-codoped hierarchically porous carbons derived from ginkgo leaf	-	KOH (6M)	330.5 Fg^{-1}	[88]
Cashew nut husk biomass waste	PTFE+AB	KOH (6M)	305.2 Fg^{-1}	[89]
KOH activated malva nut-derived microporous carbons	PTFE+AB	KOH (6M)	247 Fg^{-1}	[90]
KOH activated castor shell powder with nitrogen-rich spirulina extract	PTFE+AB	KOH (6M)	365 Fg^{-1}	[91]
Crude polysaccharide extract from waste fungal substrate	PVDF+AB	KOH (6M)	152 Fg^{-1}	[92]
Pinewood, candlenut, cedar wood and gulfweed derived porous carbon	PTFE+conductive graphite	KOH (6M)	366 Fg^{-1}	[93]
Inner wall of tracheids in wood carbon slices derived carbon nanotubes	-	Na_2SO_4 (1M)	215.3 Fg^{-1}	[94]
Tamarisk root-based honeycomb-like porous carbon	PVDF+CB	Na_2SO_4 (0.5M)	293 Fg^{-1}	[95]
Double activated lotus carbon by KOH and HNO_3	PTFE+CB	KOH (6M)	478 Fg^{-1}	[96]
Viburnum sargenti leaves derived graphitic porous carbon	PTFE+AB	KOH (6M)	612.8 Fg^{-1}	[97]
Poultry litter derived -porous super-activated carbon	-	Na_2SO_4(1M)/ KOH(1M)	229 Fg^{-1}	[98]
N-doped bamboo derived porous carbons	PTFE	KOH (6M)	209 Fg^{-1}	[99]
Chinese parasol fluff derived carbon	PVDF+CB	H_2SO_4 (2M)	682 Fg^{-1}	[100]
Millet straw activated carbon, anthracite coal activated carbon	PVDF+CB	KOH (2M)	144 Fg^{-1} 85.2 Fg^{-1}	[101]
Xanthocerassorbifolia seed derived biochar	PTFE+AB	KOH (6M)	276 Fg^{-1}	[102]
Eggplant derived carbon flakes@$NiCo_2S_4$ nanosheets	-	KOH (1M)	-	[103]
Ag-Banana BC	PVDF	Na_2SO_4 (1M)	655 Fg^{-1}	[104]
Pomelo Peel	PVDF+AB	$LiPF_6$/ethylene carbamate (1M)	297 $mAhg^{-1}$	[105]

potential window with long term cyclic stability. Pickling-SE exhibited 39.7 % more specific capacitance (Fg^{-1}) than original-SE at 1 Ag^{-1} in Li_2SO_4 (1 M) and also showed higher stability (97.2%) over 5000 cycles. This excellent electrochemical performance of pickling- SE electrode, increased with surface area and fraction of the mesopores [113]. Doping of biochar with hetero atoms can improve its electrochemical properties, which increase its applications in ESDs. Carbonization and KOH activation process of a nitrogen rich microalgae *chlorella vulgaris*

provided an activated carbon having 21.8 to 1.40 wt.% nitrogen atom content and 1210 to 2433 m^2g^{-1} SSA. This nitrogen doped activated carbon had high specific capacitance (117 Fg^{-1}) at 0.5 Ag^{-1} suggesting that the carbon materials derived from nitrogen rich microalgae have a good potential for electrochemical applications in ESDs [114]. These facts reveal that the modified biochar has promising potential for energy storage applications and it can be a highly efficient electrode material in SCs with low environmental impacts.

Conclusion and future aspects

Waste biomass could be utilized at large scale by converting it into useful, ecofriendly carbon materials such as biochar to solve the energy storage problem and this biomass conversion also creates economic opportunities, as the derived biochar is found to be cost effective. To increase the applications of biochar as energy storage material in SCs, it can be further treated with chemical modification methods. The modification of biochar through chemical activation methods and its applications in energy storage devices such as SCs has also been discussed in this review. Biochar, upgraded through diverse treatments, showed various improved properties but there is still need for further appropriate and novel treatments of biochar activation along with the improvement of existing methods because these ordinary chemical modification methods introduce some toxic chemicals into biochar moiety which are responsible for the distortion of green approach of biochar. A green chemistry approach should be applied in the chemical treatment methods of biochar so that biochar could improve its energy storage properties and remains completely as a green ecofriendly compound without harming the nature. In addition, a detailed research is required on biochar to increase its applications in ESDs.

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