

Recent advances in bio-based electrode materials in supercapacitor applications: *Energy storage materials and technologies*

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ABSTRACT

The modern world's reliance on fossil fuels has led to many issues, including rising fuel prices, pollution, climate change, and geopolitical unrest. While massive effort is required to deal with climate change comprehensively. Developing alternative energy sources and storage technologies is an important priority that can only be gained over time by reducing these issues. Because of this, recent years have seen an increase in the use of high-power and high-energy density storage systems, increasing the use of renewable energy sources or improving transportation efficiency contribute to climate change mitigation. Renewable energy resource deployment is associated with storage systems for reliable and continuous energy supply. It is essential to keep developing more efficient storage units to advance environmentally friendly technologies. Despite extensive research and development efforts, an essential upsurge in energy storage capability is required to meet future demand. In the next generation of energy storage devices, supercapacitors (SCs) seem an excellent candidate for wearable and portable electronics compared to the flexible lithium-ion batteries-based technologies. Electrochemically excellent carbon materials are required to protect the environment and develop renewable energy sources, but they are scarce. Depending on the desired carbon morphology, there are many different types of biomasses and biowaste materials from which to choose carbon precursors. The preparatory work and characterization of newly found and evolved bio-based carbon sources are discussed and summarized in this study. Precursor and nanostructure types are listed in alphabetical order. New carbon precursors with excellent electrochemical performance in energy storage applications are also discussed. Ultimately, a conclusion and an outlook from the application perspective are drawn.

Keywords

- Supercapacitors
- Bio-based amended supercapacitors
- Bio-based materials
- Electrodes
- Storage efficiency
- Supercapacitor configuration

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1. Introduction

A massive effort is required to deal comprehensively with climate change [1,2]. You can either increase the use of renewable energy sources or improve transportation efficiency to address this problem. It is one of the ways to achieve a more sustainable environment by relying more on renewable energy sources, such as electric vehicles. It is essential to keep developing more efficient storage units to advance environmentally friendly technologies [3,4]. Despite extensive research and development efforts, an important upsurge in energy storage capability is required so that it can meet the needs of the future [5].

The excellent electrochemical and physical properties of polyacrylonitrile-based carbon precursors have made it a deep-rooted and well-investigated electrode conductive material for energy storage devices. Electrochemically excellent carbon materials are required to protect the environment and develop renewable energy sources, but they are scarce. Because PAN is a carbon precursor, bio-based materials are excellent substitutes. Depending on the desired carbon morphology, there are many different types of biomasses and biowaste materials from which to

choose carbon precursors. This review discusses and summarizes the preparatory work and characterization of newly found and evolved bio-based carbon sources. Precursor and nanostructure types are listed in alphabetical order. New carbon precursors with excellent electrochemical performance in energy storage applications have also been summarized. Ultimately, a conclusion and an outlook are presented. In general, bio-based carbon-electrodes for energy-storage devices appear to be highly advantageous.

Graphene, carbon nanotubes, and conductive polymers are the most effective active materials for SCs [5,6]. It has recently been discovered that carbon electrodes made out of biomass are a potential solution due to various their minimal price, flexibility of morphologies, mixtures, and mechanical characteristics, facilitating the development of more advanced hybrid ESSs, either on or permanent. Electrodes, liquid electrolytes, and a separator are the three functional parts of a conventional energy storage unit. As ions are charged and discharged, the separator facilitates the movement of ions from one electrode to the next. The



separator works like this. Lithium-ion and supercapacitors (SCs) are the supreme researched and developed energy-storage devices in recent literature [3]. When it comes to energy density, LIBs and SCs are vastly different. The functional components of energy storage devices like these can be summarized as follows. Liquid electrolytes are advancing because of their ionic conductivity and thermal and electrochemical stabilities [4]. Separator advancements directly impact the unit's ionic resistivity and overall safety [5]. Progress in electrode technology, the sole focus of this review, affects electrochemical performance and stability directly.

Compared to conventional carbon electrode production methods, bio-bases have a significant cost advantage in producing carbon electrodes for power generation. Most biomass sources (for example, corn and rice husks) are byproducts of agriculture or industry (e.g., lignin). Additionally, most bio-waste foodstuff and plants (such as rotten fish and shrimp shells) are practically free. Bio-based materials can be carbonized in a manner that is very similar to that of polyacrylonitrile (PAN), which is important to keep in mind. PAN and bio-based precursors have the same processing costs. Efforts have been made to cut down on the time and cost of data processing. When it comes to shortening the time required for carbonization, for example, using microwave assisted-hydrothermal and microwave plasma-pyrolysis [3,4] have been reported to be effective ways to increase the output of nanofibers, as well as to reduce the carbonization process time. Thus, bio-based materials don't just serve as cheap carbon precursors; they also serve other purposes. Bio-based electrochemical behavior is yet another significant factor in deciding their viability for energy storage applications. The morphology, porosity, and pore size, specific surface area, and doping level of a carbon-based electrode are generally linked to its electrochemical performance. An unusual combination of nanostructure, porous structure, and heteroatom-doping is found in bio-based carbon electrodes [5,6].

Carbon diodes derived from renewable biomass and bio-waste are ideal to meet the needs for the extraordinary performance of energy storage. Energy storage applications can benefit from using bio-based carbon precursors and this review summarizes and discusses these processes. Based on the type of precursor and the morphology of the nanostructure, the study is laid out in outline form. Preparation methods and properties are discussed in depth for each section. The review has also discussed

and summarized carbon precursors with excellent electrochemical performance—applications for storing energy. Bio-based carbon electrodes have a bright future in applications for storing energy.

2. Materials and methods

Bio-based carbon electrodes for SCs are being investigated as a potential means of increasing the efficiency of these batteries SCs. This manuscript aims to review the scientific works to evaluate the routine of the SCs with different cost-effective bio-based carbon-electrodes and to classify the most significant effects of SCs on performance. Furthermore, this manuscript has exposed the earlier prestigious studies and several alternative descriptions given by researchers in this field. Afterward, these studies were deeply analyzed, finding research gaps and related problems that need to be solved and recommending future research guidelines. This study selects recent advances and significant contributions related to the utilization of bio-based carbon electrodes for Scs of Elsevier, Scopus and ScienceDirect, and Google Scholar databases; using the following Boolean search string: (“Electrode” OR “bio-based electrode” ((supercapacitors performance OR rate capability) AND (various types of electrode OR bio-based electrodes))). These publications report the different types of electrodes and techniques for improving the Scs performance. After ensuring relevant literature, this study incorporated some other relevant studies when reviewing studies. This review set up the following selection rules based on selected relevant literature:

- Include the accessible and most relevant study to the topic (published).
- Exclusive and latest study was preferred.

2.1. Different materials used for making supercapacitor electrode

We've compiled a list of the most important electrode materials and briefly described their properties. Carbon-based materials, metal oxides, conducting polymers, etc. In a wide range of applications, carbon-based materials are widely used. As a result of their low price and well-established industrial production methods, they are readily available. In this section, various types of carbon that are used in supercapacitors are discussed. Cyclic-voltammograms of these materials shows an almost rectangular shape like that depicted in Figure 1.

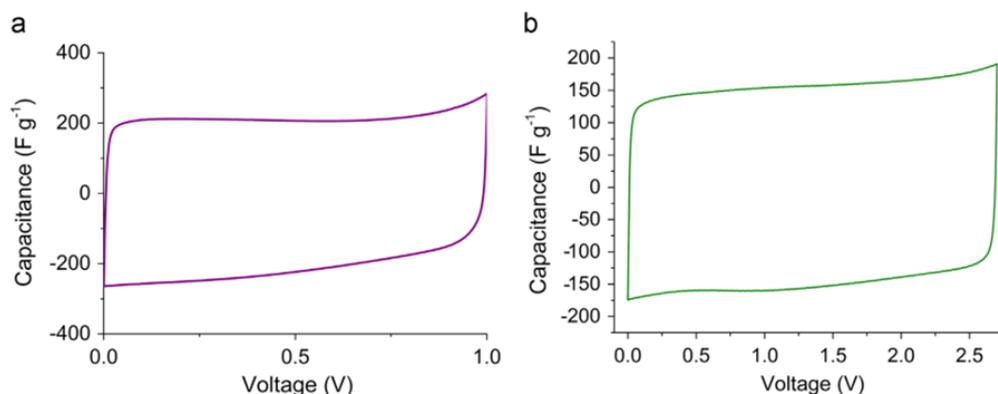


Figure 1. (a) One of two electrolytes used in this experiment: 6M KOH and (b) 1M Tetraethyl ammonium tetra fluoroborate [5].

2.2. Fabrication of electrode from activated carbon

Regarding supercapacitor electrodes, activated carbon is the most common active material because of its high surface area and low cost. This material's porosity is created by activating and carbonizing carbon-rich organic precursors. Natural renewable resources, such as coconut shells and wood, as well as fossil fuels and their derivatives, such as pitch, coal, or coke, as well as synthetic precursors, such as polymers, can all be used to produce precursors [6].

Precursors undergo thermal chemical transformation to produce amorphous carbon, while activation produces a high surface area. Through the use of physical or chemical activation, the carbon precursor grains can be partially oxidized. If you want to activate amorphous carbons that have been diversely treated with compounds such as KOH, K_2CO_3 , and CO_2 , H_2O , etc., physical activation is the best option. Carbon particles with a porous structure can be activated to form porous networks in the bulk of the carbon particles. Nano-pores can be divided into micropores (2 nm), mesopores (2–50 nm), and macropores (50–100 nm) based on their size (450 nm). To accurately measure SSA, the calculation method and the measurement conditions play a significant role. There have been reports of specific surface areas of $3000 \text{ m}^2 \text{ g}^{-1}$ [6,7], but the usable SSA is usually in the $1000\text{--}2000 \text{ m}^2 \text{ g}^{-1}$ range.

Activated carbon electrodes and organic electrolytes are used in the majority of commercially available devices. A specific capacitance of $100\text{--}120 \text{ F g}^{-1}$ [6,8] can be achieved at working voltages (2.7 V) of the cell in these devices. A few real-world examples will help clarify this. In an aqueous electrolyte, cost-effective biochar with higher carbon content was stated to have a 115 F g^{-1} capacitance [9]. With capacitance retention of 86.4 percent at 1 amp, carbon hollow-fibers attained 287 F g^{-1} [10]. 340 F g^{-1} of specific capacitance was reported in [11] for carbon prepared from sugarcane bagasse by phosphoric acid activation. Operating voltage in aqueous electrolytes is 0.9 Voltage and 300 F g^{-1} superior specific capacitance [12]. To coat current collectors, activated-carbon nanoparticles can be combined with carbon blacks and organic binders to form catalyst layer films. Because the activation process

is difficult, activated carbon powders typically have a wide distribution of pore sizes [6]. Higher temperatures or longer activation times result in larger average pores [12]. Material's SSA is under-utilized, which means that some of it do not contribute to capacitance.

2.3. Fabrication of electrode from carbide carbons (CC)

Metals can be extracted from carbides by heating them to high temperatures or carbons derived from carbides. High-temperature chlorination [13] and vacuum decomposition [14] are the two most common methods of CC production. Compared to activated carbons, SCs could benefit from carbide precursors because they allow for fine-tuning of porous networks and greater control over functional groups [14]. Carbide precursors contain a wide range of carbon atoms, and a change in synthesis temperature allows for a wide range of porous networks in CCs. It can be shown by comparing titanium and silicon carbide-derived carbons that the same synthesis temperature of $1200 \text{ }^\circ\text{C}$ leads to a narrower distribution of pores and a smaller average diameter of SiC-CC [15]. Irrespective of the precursors used, an increase in pore size is observed with an increase in synthesis temperature [14]. A temperature of more than $1300 \text{ }^\circ\text{C}$ is required for synthesis; the porous structure collapses, and graphitization occurs at lower temperatures than this [16]. Treatments such as hydrogen can improve the properties of CCs [17].

The use of CCs in supercapacitors reveals that the CC structure governs capacitance, whereas starting carbide significantly impacts rate performance. Although Titanium CCs was shown in experiments to have the highest gravimetric capacitance in KOH and organic electrolyte, SiC-CCs had the highest volumetric capacitance (126 F cm^3 in KOH and 72 F cm^3 in organic electrolyte) [15], respectively. An organic electrolyte containing $(\text{CH}_3\text{CH}_2)_3\text{CH}_3\text{NBF}_4$ as salt was found to have a specific capacitance of TiC-CC between 70 and 90 F cm^3 or between 100 and 130 F g^{-1} in another study [17]. An experiment with tailored porosity in the temperature range of $600\text{--}1200 \text{ }^\circ\text{C}$ CCs was used to study the effect on capacitance of the size of the pores. The results showed that pores smaller than 2 nm have a much greater impact on

capacitance than larger than 2 nm surface area CCs. Capacitance decreases as the temperature of CC synthesis rise, despite an increase in the specific surface area and pore volume. This suggests that pore size is the most important factor in capacitance. The synthesis temperature can also be changed to accommodate higher energy or higher power applications [18,19].

2.4. Fabrication of electrodes from Carbon nanotubes

Catalytic decomposition of certain hydrocarbons yields carbon-nanotubes (CNTs) and carbon nanofibers [18]. It is possible to control the crystalline order of different nanostructures by manipulating various parameters [20]. Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) could be synthesized using different parameters. Because of their high electrical conductivity and large accessible external surface area, these are ideal [18,21]. According to [2,20], the purity and morphology of CNTs have a significant impact their capacitance. Mesoporous electrode surfaces are most common on CNTs, and these surfaces are linked to the outside of the tubes [20].

CNT surface hydrophobicity is responsible mainly for the specific capacitance range of 20 to 80 F g⁻¹ [20] found in purified CNT powders. It is possible to increase the specific capacitance up to about 130 F g⁻¹ through subsequent oxidative processes. Pseudo-capacitance can be induced by oxidative treatments that alter the surface texture and introduce new surface functionality [7]. MWCNTs with a 250 m²/g¹ BET surface area were catalytically grown [22]. Electrodes made of freestanding mats of entangled CNTs with an increased surface area of 430 m² were formed after CNTs were treated with nitric acid. Even though it had minimal microporosity, this mat had pores with an average diameter nearly twice the diameter of the nanotubes, at 9.2 nm. Much of the nanotube mats' porosity can be attributed to the entangled network of nanotubes, which form interstitial spaces. When measured at 1 Hz, sulfuric acid's specific capacitance was found to be a double layer of 24.2 F cm² with a specific capacitance of 102 F g⁻¹. The estimated power density of this cell was over 8 kW kg⁻¹. Composites combining CNTs and conducting polymers are being developed because CNTs have a moderate capacitance due to their low SSA. CNT double layer capacitance and pseudo-capacitance of conducting polymers are combined in these composites to achieve higher capacitance than can be achieved with either of these materials alone. The conformal deposit of pseudo-capacitive material in CNTs. When a suitable monomer is chemically polymerized, a uniform coating is formed on the CNT surface [23] in order to create the composites. Polypyrrole (PPy)-electrode-deposited MWCNTs have a specific capacitance of about 170 F g⁻¹, but a cycle life of more than 100,000 cycles may not be possible due to the degradation of the polymer [23]. When SWCNTs were used in place of MWCNTs, specific capacitances of up to 265 F g¹ were achieved. The PPy in these composites also serves as a conductor, lowering the supercapacitor's ESR [23].

Overcharging or over-discharging during operation can hasten the degradation of the composite. Then carbon supported transition metal oxides can improve stability [10]. It is possible to upsurge the 30-80 F g⁻¹ of specific capacitance by adding one percent RuO₂ to the MWCNT electrode. In addition, it has an extended cycle life as compared to CNTs covered with a thin layer of conducting polymer [10].

2.5. Fabrication of electrodes from graphene

To make graphene, a one-atom-thick sheet of carbon, carbon molecules are sp² bonded together in a polyaromatic honeycomb crystal lattice. Because of its high rate and cycle capability, increased capacity, and excellent physiochemical properties, this material is well-suited for high-performance energy storage systems [24]. Its compensations include many functional groups on the material's surface, good flexibility, good conductivity (both electrical and thermal), and good conductivity.

With ionic liquid electrolytes, graphene-based SCs with superior specific capacitances (75 Fg⁻¹) and energy densities of 31.9 W h kg¹ have been reported [10], as well as 135 F g¹ in aqueous electrolyte and 99 F g¹ in organic electrolyte [10]. The highest specific capacitance ever measured in aqueous electrolytes for reduced graphene [24]. More electrical conductivity is often found in graphene, which has a theoretical surface area of 2620 square millimeters per gram. The surface-to-volume ratio is high due to the material's flexibility and structural thinness, its thermal and chemical stability, the abundance of surface functional groups, and a wide electrochemical window that enhances ion transport kinetics. Immobilization of the graphene sheets results in irreversible capacity loss, which lowers the material's initial Coulombic efficiency. The re-stocking of adjacent sheets reduces energy density due to van der Waals interactions [10].

Graphene and metal oxide composites are an excellent alternative to re-stacking graphene sheets. Because of their synergistic effect, this is advantageous for both materials. As well as increasing available surface area, metal oxides prevent graphene from adhering to one another and stacking again. To make uniformly dispersed controlled morphologies of metal oxide nanostructures, graphene aids in forming those structures while also suppressing the growth of metal oxide agglomerates in their volume. The oxygen-containing groups in graphene enable excellent electrical contact, interfacial interactions, and bonds between graphene and metal oxide. As a result, an electron conducting network and shorter ion paths will be created in the composite. Different graphene oxide electrodes are compared in [24], with three-dimensional porous network electrodes achieving 352 F g⁻¹ at 5 mV s¹ for comparison.

Composite capacitances in graphene/metal oxide materials exceed the sum of the material's individual calculations. Because of the integrated 3D structure, these composites demonstrated improved cycle, rate, energy, and

power densities. Graphene nanosheets/polyaniline, graphene/Co(OH)₂, graphene/Ni(OH)₂, graphene/CNT, and other nonmetal oxide materials (SOD4S) supported graphene [25], graphene/Si, and graphene/Co(OH)₂ were also found to have these enhancements [26]. It achieved a power density of 65.1 W h kg⁻¹ at 13kW kg⁻¹ and 82.4 W h kg⁻¹ at the same power density at the exfoliated graphene's anchored polypyrrole [27]. The graphene nanosheet-tungsten oxide composite and the ruthenium oxide-graphene hybrid material have been reported to reach 479 F g⁻¹ per hybrid material mass. Chemical doping of graphene with electron donors and acceptors is another way to enhance the electrochemical properties of graphene-based electrodes. Supercapacitors with 242 Fg⁻¹ of N-doped graphene oxide were reported in [28] to have excellent capacity retention and cyclability. Highly nitrogenated graphene oxide was found to have a capacitance of 320 F g⁻¹ in [29].

2.6. Fabrication of electrodes from mesoporous carbons

Mesoporous carbons can be produced in several ways. These structures are particularly interesting because they are able to withstand great power ratings without experiencing substantial capability degradation. Microporosity frequently has blocks that reduce ion mobility and, consequently, the electrode's power capacity. Microporosity There is no slow-moving narrow mesopores paths, so capacitance remains even when the current density increases.

To create mesoporous carbons, a variety of methods can be used. These include carbonization of thermosetting and thermodynamically unstable components, high-degree activation, catalyst-assisted activation, and aerogels and cryo gel carbonization. With these methods, you can obtain mesoporous carbons with a wide variety in terms of pore size and high microporosity [30]. The self-assembly of soft templates through co-condensation and carbonization is another method for making mesoporous carbons. The pore size and distribution can be better controlled [31]. There are no chemical interactions between carbon precursors and templates in hard template synthesis, so the result is well-defined nanostructures. The organic molecules in the soft template self-assemble into nanostructures. Mixing ratios, solvents, and temperature all influence the pore structure. A narrow pore size distribution and well-defined pore structure have been

demonstrated for mesoporous structured carbons made using these two methods [30].

Carbon synthesized by the CO₂ activation of mesopores was found in [32] to have a specific capacitance gravimetric of up to 102 Fg⁻¹. A study in [33] describes the use of rice husk as a precursor for mesoporous carbon. This material has a BET surface area of 1357 m² g⁻¹, a pore volume of 0.99 ml g⁻¹, and a mesoporosity of 44.4%. Scannable at 5 mV/s, carbon has 114 F/g⁻¹ specific capacitance in an organic electrolyte.

3. Working principal and storage mechanism of supercapacitor

A supercapacitor has many different components, as illustrated in Figure 2. These include current collectors, electrodes, electrolytes and separators. The battery's separator serves the same purpose in this application as in the battery itself. Additionally, it isolates the two electrodes to keep them from coming into contact with each other in the event of a short-circuit. A supercapacitor's electric double-layer capacitance can store electrical energy due to charge separation at the electrolyte/bath solution interface.

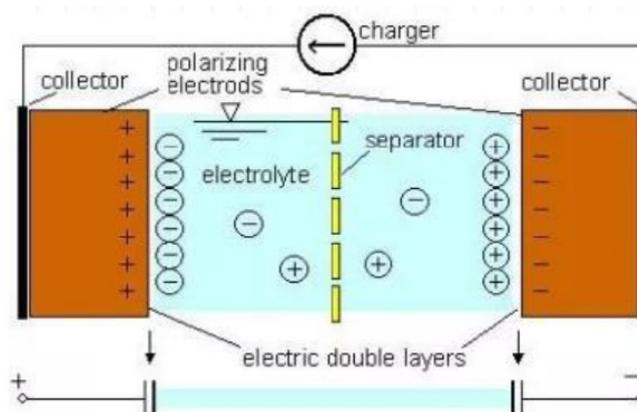


Figure 2. Working principle and storage mechanism of supercapacitor [21].

The basic functions of a supercapacitor are energy storage and distribution of ions from the electrolyte to the electrode surface area. There are three distinct types of supercapacitors, each with a distinct energy storage mechanism: A hybrid supercapacitor and a hybrid electrochemical double-layer capacitor are depicted in Figure 3.

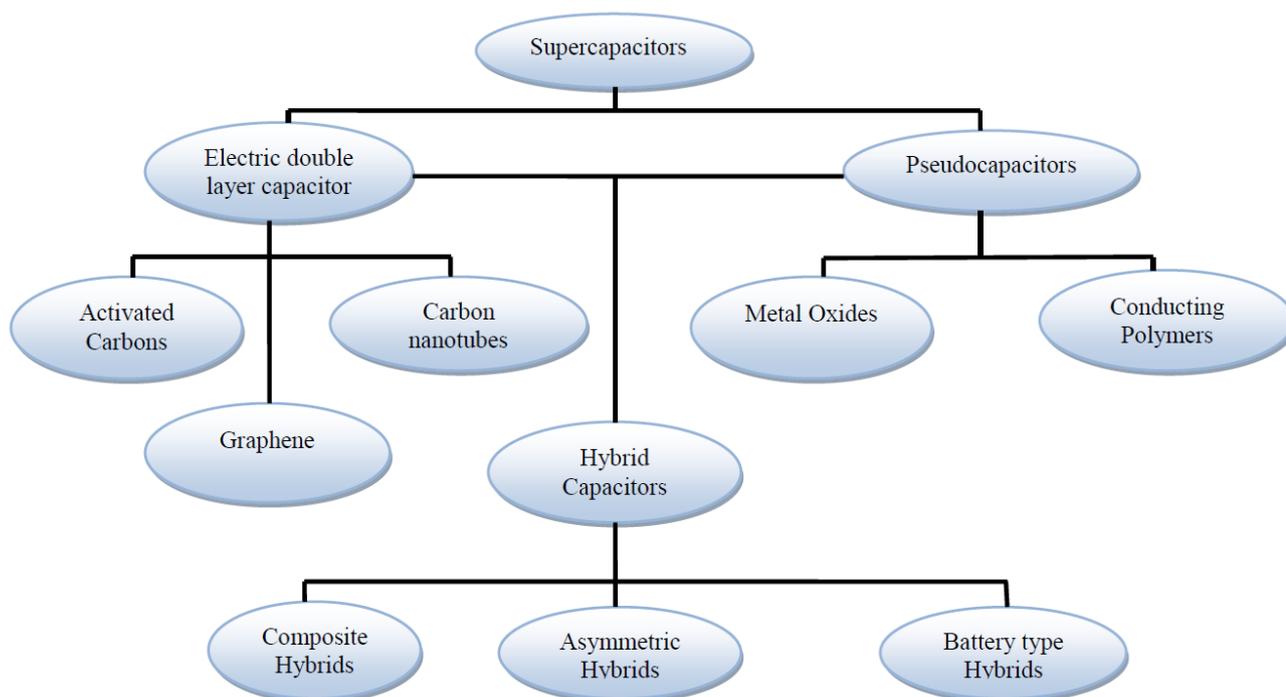


Figure 3. Storage mechanism of supercapacitor (adapted from [34]).

3.1. Capacitors with two layers of electrochemical cells (EDLCs)

The electrodes, electrolyte, and separator in an EDLC are all carbon-based materials. Either electrostatically or through a non-faradic process, no charge is transferred between the electrode and electrolyte in EDLCs. To store energy, EDLCs make use of the electrochemical double layer. When a voltage is applied to electrodes, a buildup of charge occurs. The potential difference attracts charges of the opposite polarity, which results in ions in the electrolyte diffusing over the separator and into electrode pores of the opposite polarity. Electrodes are protected from ion recombination by two layers of charge. EDLCs have a greater specific surface area and shorter electrode-to-electrode distances because of the double layer's higher energy density. Energy can be stored and delivered more quickly and efficiently with EDLC's storage mechanism. This is an important advantage. As a result of the procedure, no chemical reaction is taking place at this time. When a battery is charged or discharged, the active material in the battery expands. EDLCs, unlike batteries, can withstand millions of cycles. On the other hand, batteries have a maximum capacity of only a few thousand. Graphite anodes and high-potential cathodes in Li-ion batteries contribute to the solid electrolyte interphase, which means that no electrolyte solvent is required for charge storage [25,34]. Electrostatic surface charging means that EDLCs can only store a finite amount of energy, so researchers are working to improve energy performance and expand the temperature range in which EDLCs can operate. EDLC performance can be greatly affected by the electrolyte used.

3.2. Pseudo-capacitors

Contrasted with electrostatic charge storage devices (EDLCs). Using a faradic process, pseudo-capacitors store charge between electrodes and electrolytes [35]. Pseudo-capacitor electrode material is reduced and oxidized when a potential is applied, which results in faradic current passing through the supercapacitor cell when the double layer is charged. Comparing pseudo-capacitors to EDLCs, they have higher specific capacitance and energy densities thanks to the faradic process involved. Conducting polymers and metal oxides are two examples. Due to their faradic nature, these materials are of interest, but they also suffer from low power density and cycling stability due to the reduction-oxidation reaction, just like batteries [36–38].

3.3. Hybrid

The specific capacitance of EDLCs is larger than that of a normal CMOS device when employed as pseudo capacitance, and they also have better cycle stability and power performance. Hybrid technologies combine electrodes similar to battery electrodes with electrodes similar to capacitor electrodes in a single cell to produce a power source that is both efficient and adaptable [39,40]. Choosing the proper electrode combination can increase the cell's voltage, resulting in higher energy and power densities. Water and inorganic electrolytes have both been examined in the past using positive and negative electrodes, with both positive and negative electrodes. In contrast to EDLCs, hybrid devices have reduced cyclic stability due to the faradic electrode, making it crucial to prevent

transforming an otherwise excellent supercapacitor into a battery [41]. A distinction may be made between the three types of hybrid supercapacitors that have been explored thus far based on their electrode configurations: Asymmetric batteries are constructed from a composite material.

Composite electrodes that combine carbon-based materials with metal oxides or conducting polymers can store both physical and chemical charges. Composite electrodes can store both physical and chemical charges in a single electrode. Pseudo-capacitive materials and the electrolyte interact more readily in carbon-based materials because of the presence of a capacitive double layer of charge and the high specific surface area. A pseudo-capacitive substance increases the capacitance of composite electrodes through the Faradaic reaction [27]. Currently, binary and ternary composites are the only two types of composites commercially available on the market. Binary composites are made up of two electrode materials, whereas ternary composites are made up of three electrode materials combined to form a single electrode.

The coupling of an EDLC and a pseudo-capacitor electrode result in formation of an asymmetric hybrid that incorporates both non-faradic and faradic processes. The negative electrode is made of carbon, while the positive electrode is either made of metal oxide or a conducting polymer. Hybrid batteries combine two different electrodes similarly to asymmetric hybrids, except that the supercapacitor electrode and the battery electrode are combined to form the hybrid in this particular instance. This configuration combined the best characteristics of supercapacitors and batteries in a single cell to achieve maximum efficiency [27].

4. Bio-based material for supercapacitors electrode

For making electrodes, carbon powders of various morphologies, including nanoparticles, nanosheets, nanoplates, or random geometric nanosized configurations, are included in this section. Many bio-material resources are available, including lignin, cellulose, chitin, and protein, among others.

4.1. Lignin

Lignin, an amorphous biopolymer found in plants, serves as a binder to keep plant structures stable [36]. After cellulose, lignin is the second most prevalent natural substance. However, lignin based-carbon nanoparticles still have a relatively limited range of applications despite a recent increase in interest in the synthesis of lignin nanoparticles. This is because most synthesized lignin nanoparticles are currently colloidal, making carbonization and activation more difficult. Carbon nanoparticles derived from lignin are most commonly found as carbon dots suspended in a colloidal solution [25,35,36]. This is the most common configuration. Compared to activated polymeric-based carbon nanoparticles, the reported physical proper-

ties of these carbon nanoparticles, e.g., specific surface area, are inferior. Carbon nanoparticles with a surface area of 1100 m²/g were carbonized and activated, but the nanoparticles' structure showed signs of agglomeration and irregularity [37].

In a recent promising study, colloidal lignin-based carbon nanoparticles were recovered in solvents using a two-step process: First, the concentration of the solvent was reduced, and then the particles were isolated. For high-quality particles, the solvent concentration needed to evaporate quickly. Another study used the freeze-drying method to overcome the isolation problem, which was then stabilized and carbonized. However, the nanoparticles in this study had irregular shapes [38].

In comparison to PAN-based CNFs, lignin based-nanofibers (LCNFs) compromise a viable alternative due to their high carbon yield and abundant supply. Electrospinning can be used to make CNFs from lignin, and there are two primary methods. Lignin is used as a precursor in some nanofiber production methods, while other methods use lignin in combination with additional polymers to create a spendable blend. A high lignin concentration is essential in the first approach [41,42]. Because electrospinning is prone to clogging due to solvent evaporation, a solution with a high concentration is rarely recommended. A co-axial spinneret can be used to replace the quickly evaporating solvent and add solvent to the polymer jet, thus solving this issue. To make CNFs from lignin, co-axial electrospinning is a viable option.

The pristine lignin solution cannot be spun as easily as a mixture of lignin and auxiliary polymers created using traditional electrospinning. As a biodegradable environment-friendly precursor for CNF production, lignin is superior to synthetic polymers. Auxiliary polymers have been reduced by using lignin in greater amounts than the supplementary polymer or consuming water-soluble polymers like PVP and PVA. In light of this fact, electrospinning blends have taken over from the more complicated co-axial electrospinning setup in producing LCNF.

Only recently have carbon thin films based on lignin been studied for use in energy production. Lignin-based carbon thin films were first discovered in 2007 [41]. It was found that the film's UV adsorption and electric resistance were both affected by the film's porosity and the amount of lignin (8–20 weight percent). There has recently been an increase in the complexity of lignin-based carbon thin film structures NiCl₂ and Na₂CO₃ were added to the lignin-based carbon thin film as catalysts and activators, respectively, to alter its physical properties [42]. Lignin carbon thin film incorporated with sodium carbonate (Na₂CO₃) and nickel chloride (NiCl₂) carbonized at 1000°C possessed a specific surface area of 730 m²g⁻¹. At various stages of carbonization, gaseous Na₂CO₃ decomposition aided in forming more pores. Researchers have discovered new ways to improve the performance of lignin-based carbon thin films.

Hydrogels are 3D nanomaterials with a low density but large porosity. Research into lignin-based aerogels is widespread. Lignin aerogels are formed by controlling the molecular weight and content of lignin, as well as the mass ratios of the auxiliary resins, catalyst concentrations, and extraction methods (such as freeze-drying or CO₂ supercritical drying) [41–43]. Carbonized aerogel's gelation time and pore structure are influenced by the amount of lignin and its molecular weight [44]. Femto-Formaldehyde [43], Resorcinol-Formaldehyde [44], and NaOH/Na₂CO₃ are among the most well-studied auxiliary resin mixtures. They have a major impact on the final properties. Porosity and surface area were significantly higher in copper-doped carbon aerogels than in lignin carbon aerogels that were not copper-doped, according to one study [39].

4.2. Cellulose

A lot of cellulose is in a plant's internal structure, and it is the most abundant natural material. A green plant, such as wood pulp, has been used as a source of cellulose. It is difficult to obtain nanoparticles from cellulosic sources due to their nanostructure's fibrous and whiskery nature. There are only a few examples of random graphitic nanostructures in the proton exchange membrane fuel cell. For example, carbon nanofibers may be easier to synthesize and apply in a wide range of applications than its nanoparticle counterparts, as demonstrated in this study.

By using CNF, CC, and BCC as the main constituents of the material, it is possible to make carbon aerogels without the need for additional chemicals. To begin, cellulose nanofiber-based aerogels have been created. Nanofibers based on carbon-based carbon nanofibers and graphene oxide were carbonized, resulting in cellulose nanofiber-based reinforced reduced graphene aerogel [40]. So that nitrogen could be doped into the nanocellulose, an organic nitrogen-rich material (melamine) was mixed with the latter in a single pot. GO solution was added to the final mixture in accordance with a predetermined volume. After being dried in nitrogen liquid, the composite mixture underwent freeze-drying and carbonization at a temperature of 600 degrees Celsius. The carbonized aerogel's high nitrogen content resulted in 487 cm³/g of specific surface area per unit mass, further enhancing hydrophilicity. Hierarchical structures include cellulose-nanofiber aerogels decorated with NiCo₂S₄ nanocrystals [41]. Aerogel was formed by freeze-drying and immersion in NiCo₂S₄ precursor before the hydrothermal reaction and carbonization at 500 C. At 394 m²/g and 0.9 cm³/g, the carbon aerogel composite's specific surface area and pore volume were found to be relatively great.

Many studies have been done on nanostructured cellulosic and hierarchical carbon films based on pure cellulosic materials [43]. Using carbonization at 1000 degrees Celsius, it was possible to achieve high graphitization levels on virgin CNC film at a reasonable price. A surface area of 146 m²/g and pore sizes of 1.7–30 nm was found in the

results. Carbon nanofibers made from cellulose and filled with activated carbon were made into a flexible film using a straightforward method. A mixture of activated carbon and cellulose was vacuum-filtered before being used.

Second, the freeze-dried film was hardened by a two-hour carbonization process. Because of the hydroxyl groups on cellulose nanofibers, which may have improved the interconnection between two materials, the carbonized film maintained its integrity. As depicted in Figure 6, the film's morphology is illustrated. A carbonized film with a surface area of 1840 m²/g was created by combining activated carbon and carbonized cellulose nanofibers. These results were attributed to the carbonized film's synergistic effects due to their respective large surface areas. Cellulose nanofibrils and nanocrystals were used in a different study to create a nanostructured carbon film (CNC) [42].

4.3. Protein

Bio-based materials rich in nitrogen species are abundant in [43]. Since the extraction of protein precursors is a complex process, spherical nanoparticles are extremely rare; instead, more common structures include nonporous powder and nanoplates [44]. A protein-based carbonaceous fuel The physical properties of nanoporous-carbon precursors are exceptional [43]. Egg, silk, fish, tofu, enoki mushroom, and livestock feed like Lemna minor and enoki mushroom are protein-based carbon precursors.

Their brittle nature makes protein-based carbon aerogels a poor choice for high-temperature applications. The protein-based composite was used instead to overcome the brittleness. Examples of protein sources that can be combined with carbohydrates include ovalbumin, soy, bean flour, or regenerated silk proteins. Silk proteins regenerated from cocoons and graphene oxide were used to create a composite carbon aerogel [19]. At 800 C for 2 hrs, proteins were converted into carbon, and graphene oxide was transformed into rGO. Compared to other carbon aerogels, the composite aerogel's specific surface area, 181 m²/g, is relatively small, despite its 11 nm pore diameters. Using soy bean flour and glucose or cellulose as carbon sources, carbon aerogels can also be produced [45]. Although the specific surface area of soy protein-glucose-based carbon aerogel is acceptable at 449 m²/g, it is significantly larger in terms of both the specific surface area and total pore volume of 697 m²/g, despite having a lower nitrogen content, according to the results of these tests, which were published in the journal carbon. Fibers were formed in the carbon aerogels derived from cellulose and glucose; however, nanoparticles formed in the cellulose aerogels. There was a discrepancy between the cellulose-based carbon aerogel's end structure and its physical properties. Protein is a common building block for CNFs, but it cannot function as a standalone membrane for these cells. One solution to this problem is the creation of CNFs through the incorporation of lignin into plant proteins. However, lignin addition significantly increased the

average fiber diameter from 540 nm to 2610 nm, even though the membrane structure was preserved [46]. When carbonization occurs, proteins like protamine lose their fibril structure. As a result, adding calcium salt improved thermal stability and preserved nanofibril structure, leading to brittle CNFs as a remedy solution [47]. Another group [48] has suggested using transition metals like zinc, cobalt, and nickel to make CNFs that are both stable and flexible. After determining that the prolamin protein degradation temperature range was between 200 and 300 C, they followed a particular carbonization procedure. Initially, the sample was heated to 200 C at a rate of 5 C/min and held at that temperature for 2 hours. Second, the temperature was raised to 300 C and kept there for 4 hours using a lower heating rate of 1 C/min. Finally, the temperature was raised to 800 C and kept there for 2 hours before being allowed to cool to room temperature at a rate of 1 C/min. The Breakability and freestanding properties of protein-based CNFs remain significant challenges that need to be addressed in greater depth.

5. Role of bio-based electrode in storing mechanism

Compost and biowaste are abundant, environmentally friendly, and renewable sources of carbon-based carboxylic acid precursors. Examples of this type of material include lignocellulosic chitin and protein, which can be found in biomass and biowaste. Other non-conventional biomass options include food wastes, flowers, seeds, and plant byproduct wastes. Each material possesses a unique combination of properties after carbonization when it comes to high-performance electrodes for energy storage devices such as lithium-ion batteries and supercapacitors [49].

Batteries are being pushed to their limits by electric automobiles and the great performance of electronic devices, which are causing a paradigm shift. Material preparation protocols for carbon-based electrode energy storage devices must be developed to meet this technological demand for high electrochemical performance. Increasing the specific-surface area, enhancing physical structure, and doping individual atoms or heteroatoms are all part of these protocols. The following sections review bio-based carbon electrode performance in rechargeable batteries and SCs.

These materials have large specific surface areas that can be used for high electrochemical performance. More ions can be stored in the electrolyte solution faster and diffuse more efficiently with a great specific-surface area electrode in energy uses [50]. Electrodes with high specific surface areas, such as graphene or PAN, are high-performance electrodes. As described in the previous section, carbon-based electrodes can be improved by adding nanoparticles to increase surface roughness. Bio-based electrodes are ideal for this application because of their large specific surface area.

5.1. Role of bio-based electrode in storage efficiency of SCs

As a result of their chemical and electrochemical stability, as well as their capacity for charge storage, carbon-based materials have been widely employed as functional electrodes in energy storage devices [51]. SCs are additional storage devices that can deliver high power in a short period. One of the most notable shortcomings of storage batteries is that they do not have a high degree of cycling stability. Generally speaking, supercapacitors are composed of three components: electrodes, electrolyte, and separator. As the electrodes are being charged and discharged, the electrolyte and separator keep the ions floating and the electrodes separated. For electrochemical performance, the electrodes are the most critical functional component. There are numerous advantages to using carbon-based electrodes, including excellent physical and chemical properties, in SCs. Recent research in SCs has focused on developing electrodes derived from renewable sources. Making high-performance electrodes from biomass or biowaste with active materials and a high specific surface area, controlled physical structure, doping with various atoms, and enhanced pseudo-capacitance activity is nearly universally the same no matter where you begin. At 421 Fg^{-1} , a high capacitance was achieved by using an activated eggshell as an electrode in a supercapacitor with the remaining egg components as an electrolyte and separator [51]. High surface areas and self-doped nitrogen, oxygen, and Sulphur species may have triggered pseudo-capacitance activity. Using walnut shell-based electrodes with an ultrahigh specific surface area and tuned pore size, a capacity of 216 Fg^{-1} with a high energy density of 48 Whkg^{-1} and an ultrahigh power density of 100 KWkg^{-1} was achieved. A walnut shell electrode outperforms its activated carbon counterpart in electrochemical performance, as shown in Figure 4. The large surface area allowed for better ion and electron transport, and the tuned pores allowed for the accumulation of charged particles. Electrodes made from biomass and biowaste materials such as aloe vera and cabbage are delivering high power density and energy density in recent efforts. The electrochemical properties of bio-based carbon materials. In addition to providing new ion diffusion pathways and charge storage space, the inner structure's nitrogen and oxygen species also enhance the electrode-to-electrolyte interface. By increasing electronic conductivity, nitrogen enhances pseudo-capacitance activities.

SCs have a much higher percentage of electrodes without binders than batteries. Electrospun membranes and aerogels are two of the most commonly used methods for making a binder-free electrode. Moreover, these materials can be further improved by incorporating additional additives, making them even more effective. It was claimed that electrospun electrodes integrating graphene-nanosheets in the lignin PAN-based electrospun electrode were able to upsurge the surface area and commentator nitrogen and Sulphur species.

The composite electrodes generated 9.3 Wh kg^{-1} compared to 4.1 Wh kg^{-1} for the pristine electrodes. Using nanocrystals of Co_3O_4 nanocrystals in aloe-based aerogel electrodes provides excellent cycling stability over 10,000 cycles and an energy density of 68.2 WhKg^{-1} [51].

Additional testing has shown that SnO_2 and NiCo_2S_4 can improve the performance of SCs. Despite significant efforts to improve the current SC state, energy density of carbon electrodes derived from biomass and biowaste resources still needs to be improved.

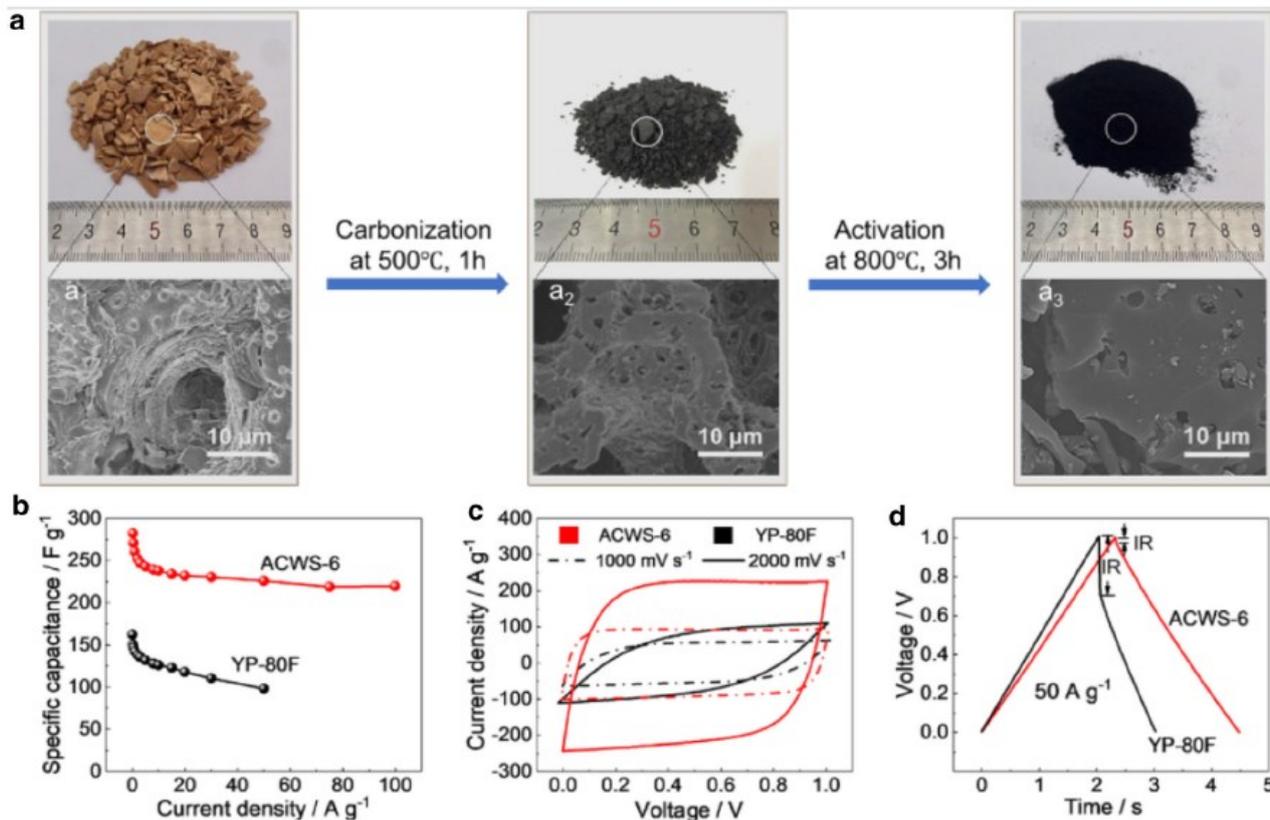


Figure 4. Prepared walnut shell electrode performance compared to activated carbon [51].

6. Conclusion and future outlook

In contrast to petroleum-based carbon precursors, bio-based carbon precursors are environmentally friendly. Bio-based carbon precursors are low-cost because they are widely available in nature. On the other hand, the physical properties of bio-based carbon electrodes make them ideal for energy storage. Classifying and categorizing the nanostructured morphology and the natural origin of bio-based carbon precursors used in energy storage applications is possible. Carbon precursors include proteins (e.g., egg) and other uncommon substances like lignin, cellulose, chitin, and chitosan. The four morphological categories summarize and critically evaluate each material's methodology, preparation protocols, morphology, physical properties, and doping mechanisms. A recent study on bio-based electrodes for rechargeable batteries and supercapacitors has found that both can benefit from the latest developments in this field. The entire review serves as a concise guide for designing high-performance bio-based carbon electrodes. Novel nanostructured bio-based electrodes capable of delivering high electrochemical

performance in batteries and supercapacitors have attracted much interest.

Nanoporous electrodes with a specific surface area greater than $1000 \text{ m}^2/\text{g}$ and even exceeding $3000 \text{ m}^2/\text{g}$ have been developed by some researchers. These physical properties result from novel preparation protocols combined with some activation agents, depending on the initial precursor. A separate group of researchers was developing heteroatoms and self-doped carbon electrodes to demonstrate their feasibility in bio-based carbon electrodes. Biomass material's bone structure can either preserve existing species (such as nitrogen and oxygen groups), or new species can be introduced by incorporating different substances. An increase in pseudo-capacitance activity and an increase in electrochemical stability can be achieved thanks to the exceptional properties of these materials. This has led to the development of carbon electrodes made from bio-based materials that perform exceptionally healthy.

Despite massive efforts to use bio-based carbon precursors as high-performance electrodes, rechargeable batteries and supercapacitors still need to be improved to meet

the ever-increasing demands of tomorrow. The following issues must be addressed to enhance the status of bio-based carbon electrodes in energy applications: Biomass and biowaste have low carbon yields compared to synthetic materials. Increasing the amount of carbon that can be extracted from a given amount of coal or natural gas can reduce the cost of energy devices in various ways. This can be done by using additives that reduce the loss of specific carbon species during the process of carbonization. Surface area, pore size, and doping should be studied more closely to develop electrodes with the best possible physical properties for optimal electrochemical performance. Organic binders are required to carbonize some biomass and biowaste materials before they can be used as functional electrodes.

On the other hand, the overall performance of the electrode suffers as a result of this approach. To solve this issue, devise new and straightforward methods for fabricating freestanding electrodes from self-doping materials." Bio-based carbon electrodes have unique physical and chemical properties for high-performance electrochemical applications. Before electrodes can be used to their full potential in energy storage applications, much work must be done.

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