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Review Article

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Current Approaches to Agricultural Waste Transformation into Bioelectrodes and Hybrid Electrodes: A Review

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Abstract

Microbial electrochemical technologies (METs) offer promising avenues for sustainable energy production and environmental remediation. However, the conventional electrodes used in METs pose limitations in terms of cost, availability, and environmental impact. Various electrode materials are being explored to overcome these challenges, with a particular focus on utilizing agricultural waste as substrates. Agricultural waste materials, including crop residues and food waste, possess a significant carbon content and essential elements, making them promising candidates for investigation as potential sources for electrode production. Various conversion methods of biochar like carbonization, pyrolysis, and chemical activation, are used for converting agricultural waste into functional electrode materials followed up with optimisation of fabrication parameters like electrochemical performance, conductivity, and stability of hybrid electrodes. This review provides an elaborative discussion of electrode fabrication techniques and the development of hybrid electrodes using agricultural waste as an alternative to conventional electrodes. It also highlights the recent case studies and research advancements on successful applications of bioelectrodes in METs. Utilizing waste materials enables sustainable energy production and addresses waste management challenges. Towards the end, the perspective on scaling up these technologies for real-world implementation along with economic and environmental considerations has been outlined. This paper serves as a valuable resource for researchers, engineers, and policymakers interested in advancing METs through innovative conversions of waste to bioelectrodes.

Keywords

Agricultural waste, Biochar, Bioelectrodes, Biomass, Hybrid electrodes, Microbial electrochemical technology

Introduction

Agricultural waste is a valuable resource with diverse applications. It can be used to produce bioenergy through processes like anaerobic digestion and fermentation, providing renewable sources of fuel. In recent years, there has been a major surge in interest directed toward the usage of natural resources, such as biomass and agricultural waste, as sources of carbon that are both cost-effective and environmentally friendly [1]. The investigation of transforming these resources into nanoscale goods with remarkable characteristics for diverse applications, including electrical devices, water purification, and energy systems, is being conducted by researchers and industries. METs combines microbiology and electrochemistry to utilize microorganisms' electron transfer capabilities for applications like wastewater treatment, bioenergy production, and biosensors, promising sustainable and environmentally friendly solutions. One of the primary objectives is to identify affordable alternative precursors to produce graphene-like materials utilized in METs. Notably, considerable progress has been made in synthesizing nano scale products using agricultural waste and a diverse range of raw materials. In the pursuit of sustainable practices and the promotion of the bioeconomy, extensive research has focused on modifying and seeking alternatives to commercial components used in METs [2]. Agricultural waste, due to its abundance and easy accessibility, presents an exciting opportunity for the creation of extensive METs. The utilization of these METs exhibits promising capabilities in effectively eliminating organic substances, nutrients, contaminants, and generating bioenergy from wastewater in a simultaneous manner. The focus has switched towards the application of biochar derived from agricultural waste as an anode material due to its advantageous surface area that facilitates microbial colonization, in order to harness the benefits of agricultural waste. The objective of this technique is to tackle the difficulties linked to the high costs of carbon- and metal-based electrodes and catalysts that are frequently employed in METs [3].

The review encompasses an analysis of different agricultural biomass sources for biochar production and assesses the performance of biochar-based electrodes compared to costly carbon- and metal-based counterparts. The objective is to evaluate the feasibility and effectiveness of employing agricultural waste as a viable solution to overcome the challenges in electrode materials for METs. By capitalizing on the potential of agricultural waste, researchers aim to develop bio electrodes and hybrid electrodes. Bioelectrodes leverage biochar derived from agricultural biomass, offering a sustainable and cost-effective alternative to traditional electrodes. These bio electrodes provide a favourable environment for microbial growth and enhanced performance in METs [4]. Furthermore, hybrid electrodes are designed to enhance their electrochemical characteristics and stability by integrating biochar with other substances, such as conducting polymers or metal oxides. The transformation of agricultural waste into bio electrodes and hybrid electrodes presents a promising approach to address the challenges associated with expensive electrode materials used in METs. By utilizing biochar derived from agricultural biomass, researchers contribute to the sustainable development of METs. These technological developments facilitate the development of cost-effective and environmentally sustainable solutions, hence improving the efficiency and affordability of METs across a range of applications [5]. This research demonstrates the potential of agricultural waste as a useful material in the production of electrodes, lending credence to the use of renewable resources and the promotion of sustainable practices.

Types of Agriculture Waste Used as Electrode Materials

The research focus on electrode materials has been experiencing a consistent rise in attention due to its significant impact on the performance of METs. Carbon-based compounds are commonly used as traditional electrode materials (e.g., carbon cloth, carbon felt, graphite, carbon nanotubes, and activated carbon), metals, metal oxides (such as platinum, gold, nickel, SnO_2, and TiO_2), and conducting polymers [6]. However, recent attention has been directed towards environmentally friendly carbon materials obtained from agricultural waste to alleviate the adverse effects caused by the accumulation of agro-industrial waste. Cellulose, hemicellulose, and lignin are prominent constituents of agricultural waste. A lot is relying on how much cellulose, hemicellulose, and lignin can be extracted from agricultural waste for use in bioelectrodes and hybrid electrodes [7]. Cellulose, being a predominant constituent of the cellular walls of plants, serves the purpose of furnishing structural reinforcement. The existence of cellulose in agricultural waste biomass presents a potential avenue for the extraction and modification of cellulose to create bioelectrodes. The integration of cellulose-based materials has the potential to enhance the mechanical strength and stability of the electrode. Hemicellulose, an additional constituent of biomass derived from agricultural waste, is a complex polymer characterized by its branching structure and composed of diverse sugar monomers. Its utilization in bioelectrodes holds promise for enhancing their electrochemical properties. The enhancement of electrode conductivity and charge transfer capabilities can be achieved by the modification and integration of hemicellulose. Lignin, a complex aromatic polymer, has a notable impact on augmenting the structural integrity and mechanical robustness of plant tissues. Within the domain of bioelectrodes and hybrid electrodes, lignin has the potential to play a significant role in enhancing their mechanical stability and durability. Incorporating lignin-based materials in electrode fabrication can enhance their resistance to degradation and prolong their lifespan [8].

The varying proportions of cellulose, hemicellulose, and lignin found in agricultural waste biomass offer potential avenues for customizing the characteristics of bioelectrodes and hybrid electrodes. These proportions change across different types of agricultural waste. The optimization of individual applications can be achieved by modifying the composition and ratios of the components, thereby enhancing the electrical conductivity, surface area, porosity, and mechanical strength of the electrodes. This modification facilitates the enhancement of electrode performance, stability, and efficiency in metal electrodeposition techniques and various other electrochemical applications [4].

The utilization of agricultural waste has become increasingly significant in the creation of nanoscale products, with a particular focus on the manufacturing of materials based on graphene. Reduced graphene oxide has garnered considerable interest within the scientific community owing to its remarkable characteristics in the fields of electronics and energy devices. Reduced graphene oxide is comprised of a monolayer formed of carbon atoms that are sp2 hybridized and organized in a hexagonal lattice structure. This material has remarkable qualities such as a wide surface area, superior electrical conductivity, chemical stability, and mechanical resilience. These characteristics contribute to the material's overall effectiveness [9]. The notable attributes of these materials have garnered the attention of scholars and have been utilized in diverse domains, including ultra-filtration, wastewater management, photocatalysis, as well as energy storage and conversion apparatuses such as supercapacitors, solar cells, fuel cells, and batteries [10].

In recent times, there has been a growing trend in utilizing agricultural waste biomass as precursor materials, namely for the manufacturing of electrode and membrane materials. These materials are employed in the creation of porous carbons, which find application in electric double-layer capacitors and METs have gained significant traction [11]. Various sources of agricultural waste, including coconut shell, waste coffee beans, alfalfa leaves waste, coconut shell, sugarcane bagasse, rice husk, olive mill seed, and coffee endocarp, have been investigated. These biomass sources offer advantages such as abundant availability and low cost. As agricultural activities continue to grow globally, the generation of agricultural waste biomass also increases. However, finding alternative uses for these wastes poses challenges, as improper disposal can lead to environmental issues. This paper presents a comprehensive analysis of experimental data sourced from several studies, aiming to explore the viability of utilizing agricultural biomass leftovers as potential precursors for activated carbon electrodes in the context of supercapacitor applications. In addition, the review investigates the effect of surface modification procedures on activated carbons, providing valuable insight into methods for enhancing their performance [12].

Conversion of Agricultural Waste to Biochar

Biochar, an essential product obtained from thermochemical processes of biomass, holds significant importance in the functioning of METs. Several factors affect the efficacy of biochar in METs, including the biomass source (such as lignocellulose, cellulose, hemicellulose, and lignin) and the fabrication techniques, which typically involve elevated temperatures and variable residence times [13].

Thermal Conversion Methods

Biochar's reduced weight is a direct outcome of the process variables that govern the transformation of plant biomass into biochar. This weight loss is primarily attributed to the evaporation of water at temperatures around 100 °C. After that, the weight reduction continues due to the breakdown of cellulose, hemicellulose, and lignin at temperatures above 220 °C. Ultimately, additional weight loss is induced through the combustion of carbonaceous remnants [14]. The methods of thermochemical conversion and the process conditions connected with them are detailed in figure 1.

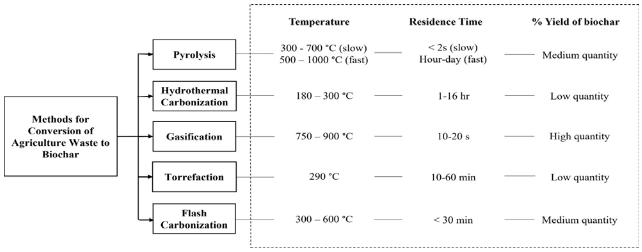

Figure 1: Thermochemical conversion techniques and their process conditions.

Pyrolysis

In the absence of oxygen, heating to temperatures between 250 and 900 °C causes a degradation process known as pyrolysis. When waste biomass is pyrolyzed, it can result in the production of beneficial byproducts including charcoal, syngas, and bio-oil. During pyrolysis, the lignocellulosic components go through several processes, such as depolymerization, fragmentation, and cross-linking, at specified temperature thresholds. These processes occur when the temperature reaches a certain level. These reactions result in products in a wide range of states, from solid to liquid to gas. C1-C2 hydrocarbons (syngas) and carbon dioxide, carbon monoxide, hydrogen, and char (solid) are the products that remain after combustion [15]. Fast pyrolysis and slow pyrolysis are the two main types of pyrolysis, and they differ in terms of heating rates, temperatures, residence periods, and pressure conditions. Fast pyrolysis, characterized by its rapid thermochemical transformation process, effectively converts solid biomass into liquid bio-oil, rendering it highly suitable for a range of energy-related applications. In fast pyrolysis, biomass particles are heated at rates that are greater than 100 °C/min. During this process, the contact time between the biomass and the pyrolysis vapors is kept to a minimum (between 0.5 and 2 s), and the temperature is kept high but not excessive (between 400 and 600 °C). To ensure the creation of bio-oil of a high-quality, it is vital to reduce the total amount of time that vapor is exposed to temperatures in the high-temperature zone as much as possible. Extinguishing vapor quickly or bringing the temperature down are both viable options for achieving this goal [16]. When compared to other pyrolysis procedures, slow pyrolysis, which comprises a moderate heating rate (5 - 7 °C/min) and extended residence times (over 1 h), results in a larger char yield. Due to the biochar's extended residence duration, which enables a more complete biomass conversion and increased carbon retention, it is beneficial for soil improvement. Biochar can be produced from the three fundamental components of biomass, which are referred to collectively as cellulose, hemicellulose, and lignin. This transformation can take place in a broad variety of reaction conditions and by a variety of processes [17].

Cellulose decomposition

Two different reactions take place during the breakdown of cellulose. These reactions are known as slow pyrolysis and fast pyrolysis. The breakdown of cellulose and the synthesis of levoglucosan are both products of slow pyrolysis that occur when the residence time is prolonged, and the heating rate is lowered. Levoglucosan can undergo dehydration, which would result in the production of hydroxymethyl furfural. Depending on the parameters of the reaction, hydroxymethyl furfural can either break down into bio-oil and syngas or continue to undergo other reactions such as aromatization, condensation, and polymerization, which ultimately result in the creation of solid biochar [18].

Hemicellulose decomposition

Hemicellulose also undergoes depolymerization, resulting in the formation of oligosaccharides. This process involves several reactions, including intramolecular rearrangement, decarboxylation, depolymerization, and aromatization. The compounds produced during hemicellulose decomposition can contribute to the formation of biochar or decompose into syngas and bio-oil [17].

Lignin decomposition

The mechanism of lignin degradation is more complicated than that of cellulose and hemicellulose degradation, respectively. The production of free radicals is the first step in the process that leads to the breakdown of lignin. This step involves the cleavage of the -O-4 lignin bond. These radicals engage in interactions with other molecular entities, which results in the capture of protons and the generation of molecules that have been deconstructed. Free radicals can multiply by participating in chain reactions with other molecules, which can affect the total degradation of lignin [15].

Hydrothermal carbonization

Hydrothermal carbonization is an effective and cost-efficient method for generating biochar, offering several advantages compared to dry processes like pyrolysis and gasification. It involves blending biomass with water and subjecting the mixture to increasing temperatures in a closed reactor. The specific products obtained depend on the temperature range employed during the process. At temperatures below 250 °C, hydrothermal carbonization results in the production of biochar. When temperatures range from 250 to 400 °C, hydrothermal liquefaction occurs, leading to the formation of bio-oil. At temperatures above 400 °C, hydrothermal gasification takes place, generating gaseous products such as carbon monoxide, carbon dioxide, hydrogen, and methane [19]. During hydrothermal carbonization, the biomass undergoes a series of reactions. Initially, hydrolysis occurs, which involves dehydration, fragmentation, and isomerization, leading to the formation of intermediate products such as 5-hydroxymethylfurfural and its derivatives. Following that, these intermediate substances experience subsequent conversions via consolidation, polymerization, and intramolecular desiccation, ultimately culminating in the generation of hydrochar. Lignin, known for its high molecular weight and complex structure, undergoes decomposition via dealkylation and hydrolysis reactions. This process gives rise to phenolic products including phenols, catechols, and syringols. As the intermediates engage in repolymerization and cross-linking reactions, char is ultimately produced. In addition, lignin elements that are insoluble in the liquid phase go through a process that is analogous to pyrolysis, which results in the formation of hydrochar [20]. Overall, hydrothermal carbonization provides a valuable approach for converting biomass into biochar, offering versatility in terms of product composition and the potential to optimize the process conditions for desired outcomes.

Gasification

In gasification, carbonaceous materials are converted to syngas and other gaseous products by a thermochemical process. Syngas is a combination of several gases, including hydrocarbons, carbon monoxide, carbon dioxide, methane, trace amounts of hydrogen, and hydrogen itself. High temperatures, in conjunction with gasification agents such as oxygen, air, or vapor, are employed to bring about this change. The chemical makeup of the syngas is significantly influenced by temperature, which is an important factor in the process [21]. The amount of methane, carbon dioxide, and hydrocarbons in the syngas can be decreased while the amount of carbon monoxide and hydrogen produced can be increased, according to studies. Syngas, primarily composed of carbon monoxide and hydrogen, are produced with greater efficiency at higher temperatures during the gasification process. It is important to highlight that the yield of syngas is much higher than that of the byproduct solid char. Gasification offers a viable method for converting carbonaceous materials into syngas, which can serve as a versatile energy source. By carefully controlling the process conditions and selecting suitable gasification agents, the production of syngas with desired compositions can be achieved for various applications [22].

Torrefaction and flash carbonization

Torrefaction is a nascent technique utilized to produce charcoal possessing distinct characteristics. Mild pyrolysis refers to the thermal treatment of biomass at moderate heating rates. During the process of torrefaction, biomass is subjected to an environment of inert air at around 300 °C, resulting in the removal of oxygen, moisture, and carbon dioxide. Several different pathways break down biomass, and each of them contributes to a different change in the characteristics of the material. Their characteristics include things like particle size, moisture content, surface area, heating rate, and energy density [23]. Incomplete pyrolysis characterizes the torrefaction mechanism, which takes place between 200 and 300 °C, with residence times of less than 30 minutes and heating rates of less than 50 °C/min. The area must be completely devoid of oxygen during this process. Drying itself can be broken down into pre-drying and post-drying phases, and the entire dry torrefaction process can be broken down into heating, drying, torrefaction, and chilling. The final product of the entire torrefaction process is biochar with desirable qualities, which is produced through the sequential processes [17].

Activation Methods for the Preparation of Activated Carbon

The process for producing activated carbon consists of two primary processes, which are referred to as carbonization and activation respectively. To begin the process of carbonization, a precursor substance must first be heated to a high temperature and then kept in an atmosphere devoid of oxygen. The first stage is followed by activation, which is a controlled thermal breakdown process that further converts the carbonaceous material into activated carbon. Activation comes after this initial step. Chemical activation, physical activation, and microwave-induced activation are some of the methods that can be utilized to improve the porosity and surface area of activated carbon material. Other activation methods include irradiation with microwaves. The production of activated carbon with the desired characteristics is greatly aided by the processes that have been described above [24].

Physical activation

Physical activation, also referred to as thermal activation, comprises two essential stages: carbonization and activation. The carbonaceous feedstock undergoes an initial carbonization step within the temperature range of 400 °C to 850 °C. After carbonization, controlled gasification ensues, employing oxidizing agents like carbon dioxide, air, or steam for the activation process. Carbon dioxide is often the preferred activator due to its comparatively sluggish reaction kinetics, typically occurring at around 800 °C. This reduced reaction rate allows for enhanced regulation of the activation procedure, thereby enabling the attainment of desired results in terms of porosity and carbon structure evolution [25]. The selection of the activating agent is contingent upon the specific precursor material utilized, as distinct precursor materials want distinct activating agents to attain a heightened surface area in the resulting activated carbon product. The primary objective of the activation approach is to increase porosity by removing carbon and volatile components, leading to an increase in surface area and pore volume. The quality of activated carbon is determined by several parameters, including the temperature and duration of the activation process, the rate at which gas is discharged, and the specific type of furnace that is utilized. Careful control of these parameters is crucial in obtaining activated carbon with desirable characteristics. Various materials, including tea leaves waste, corncob, sugarcane bagasse ash, and alfalfa leaves ash, have been studied using physical activation methods [26].

Chemical activation

In the chemical activation procedure, the precursor substance is combined with several activating agents, such as potassium hydroxide (KOH), zinc chloride ($ZnCl_2$), sodium hydroxide (NaOH), potassium carbonate (K_2CO_3), phosphoric acid (H_3PO_4), and ferric chloride ($FeCl_3$). These chemicals serve the dual function of acting as both dehydrating agents and oxidants. Chemical activation encompasses the simultaneous processes of carbonization and activation, typically conducted within a temperature range spanning from 300 to 950 °C. The approach indicated above has a significant influence on the process of pyrolytic breakdown, leading to the formation of a porous structure and increased production of carbon. Commonly employed activating agents in chemical activation include KOH and $ZnCl_2$. Chemical activation is a method employed to generate activated carbons that possess a substantial surface area. However, this particular process is characterized by its time-intensive nature and high cost, primarily attributed to the requirement of subsequent washing procedures to eliminate leftover reactants and inorganic impurities, such as ash [27]. According to [26], chemical activation is a technique utilized to produce activated carbons that exhibit a significant surface area. Nevertheless, this specific approach is distinguished by its time-consuming quality and substantial expense, principally due to the necessity of additional washing protocols aimed at removing residual reactants and inorganic impurities, such as ash, which exhibit noteworthy magnitudes reaching as high as 2959 m^2/g, accompanied by significant pore volumes. These outcomes emphasize the influence of biochar manufacturing methods and the presence of ash on the microstructural attributes of activated carbon.

Microwave-induced/assisted activation

Microwave-induced or microwave-assisted activation is a heating process that utilizes microwave energy for the activation of carbon. Unlike conventional heating methods, microwave heating directly supplies energy to the carbon bed through dipole rotation and ionic conduction within the particles. This methodology effectively tackles the obstacles linked to thermal gradients and presents numerous benefits. The utilization of microwave heating in the production of activated carbons offers notable benefits as compared to traditional heating techniques [28]. In contrast to conventional heating methods, microwave heating induces a counterintuitive thermal gradient that extends from the inner regions to the cooler surface of char particles. Therefore, there is an increase in efficiency and speed of reactions, reduction in processing durations, and conservation of energy. Microwave irradiation provides internal and volumetric heating, immediate on-off control, rapid and targeted heating, enhanced safety and automation, compact configuration, and improved overall efficiency. As a result, microwave heating has gained attention for applications such as liquid purification and the fabrication of supercapacitor electrodes [26].

Surface Modification of Activated Carbon

The shape and chemical composition of carbon compounds are crucial factors that significantly impact the electrochemical behavior of these substances. Activated carbons can be tailored for specific applications by adjusting activation conditions to achieve desired proportions of micro-, meso-, and macropores. Surface functional groups present in carbon materials can be altered through thermal and chemical post-treatment procedures, resulting in modifications to their double-layer properties [29]. The chemical composition of activated carbon comprises various surface oxygen functional groups, namely phenol groups, carboxylic groups, lactone groups, carbonyl groups, pyrone groups, ether groups, chromene groups, and quinone groups. The aforementioned groups are present inside activated carbon. These functional groups, categorized as acidic, basic, or neutral, contribute to the surface chemical heterogeneity of activated carbon, which is influenced by elements such as oxygen, hydrogen, nitrogen, sulfur, halogens, and phosphorus [30]. For surface modification, thermal treatments such as conventional or microwave heating are utilized, and chemical treatments employing chemicals such as nitric acid, hydrogen peroxide, sulfuric acid, ammonium peroxydisulfate, and ammonia water have been researched. The surface basic and acidic groups are affected as a result of these alterations. In summary, texture and surface chemistry can be customized through thermal and chemical treatments, influencing the electrochemical properties of activated carbon [26].

Techniques for Characterization of Biochar-based Electrodes

Various analytical techniques can be utilized to describe electrodes that are generated from biochar obtained from agricultural waste. These approaches can also be utilised to assess the electrochemical effectiveness of these electrodes in the context of METs. Cyclic voltammetry, linear sweep voltammetry and electrochemical impedance spectroscopy are often utilized techniques in the assessment of electrocatalytic efficiency, examination of oxidation-reduction mechanisms, characterization of cathodes and catalysts, and investigation of electron transfer kinetics. The analysis of electrode surface morphologies and specific surface areas can be conducted through the utilization of several techniques, including scanning electron microscopy and the Brunauer-Emmett-Teller method [31]. These methodologies offer significant insights into the characteristics of surface roughness and porous texture exhibited by the electrodes. For the examination of functional groups, internal structure, and composition, additional analytical methods such as X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy are utilized [32]. Techniques such as linear sweep voltammetry and Tafel plots aid in evaluating the efficacy of catalysts and studying the kinetics of electrocatalytic reactions. Applying coatings to catalysts can enhance the sluggish oxidation reduction rate (ORR) at the cathode, aiming for complete utilization of O_2 and increased voltage generation while minimizing the production of detrimental H_2O_2. Methods that can be used for the evaluation of the effective catalytic surface area include the rotating disk electrode and the rotation ring-disk electrode. Both methods revolve around rotating electrodes. The Koutecky-Levich equation is commonly employed to quantify the number of electron transfers (n) occurring in electrolytes saturated with O_2. The methods provide significant insights into the fundamental response process [33].

Agricultural Waste Derived Hybrid Electrodes for Electrochemical Devices: A Brief Overview

A hybrid electrode commonly integrates organic agricultural waste materials with inorganic constituents or conductive additions, such as carbon-based compounds like graphene and carbon nanotubes. The incorporation of both organic and inorganic constituents in the electrode architecture leads to an enhancement in electrical conductivity and overall operational efficiency. The surface area and porosity of hybrid electrodes play a vital role in the operational efficacy of various electrochemical devices, including batteries, supercapacitors, and sensors. These hybrid electrode materials have been produced using particular synthesis techniques. These materials are produced through the carbonization of biomass waste, primarily employing established techniques like the hydrothermal approach. To enhance the electrochemical characteristics of porous carbon structures, the incorporation of heteroatoms (such as nitrogen, sulfur, and phosphorus) is subsequently implemented. Porous carbon compounds are often subjected to the utilization of common chemicals, such as H_3PO_4, to enhance their refinement and activation [34]. Furthermore, the integration of heteroatom-doped porous carbons with metal oxides and sulfides is achieved to generate nanocomposites using environmentally benign chemical routes, including hydrothermal/solvothermal methods, layer-by-layer deposition, and drop casting. Flexible electrodes are fabricated using nanocomposites consisting of polymeric frameworks and functional two-dimensional nanomaterials, including graphene, MXene, few-layer boron nitride, and other similar materials [35]. Additionally, the functionalization of porous nanomaterials has received extensive attention in research to further enhance the efficiency of electrochemical devices [34].

Performance Evaluation in MET

To promote sustainable development in METs and leverage the bioeconomy, researchers have been exploring alternatives to commercial components. The researchers are presently investigating the application of agricultural waste, specifically biochar derived from waste products, as potential anode materials in METs. The utilization of biochar-based anodes presents a cost-effective alternative due to their advantageous surface area that promotes microbial proliferation. This section provides an overview of recent research conducted on biochar-based anodes, cathodes, and electrocatalysts derived from agricultural biomass. The objective of this study is to emphasize the possible utilization of agricultural waste as a strategy for addressing the challenges related to expensive carbon and metal-based electrodes and catalysts in METs [36].

Anodes

The selection of anodes for METs should prioritize their biocompatibility, effectiveness, and adaptability to MET applications (Figure 2a). Agricultural waste, which contains abundant lignocellulose, holds significant potential for producing porous carbon materials with diverse uses in water treatment, renewable energy storage, and catalytic processes [37]. Biochar with both high aromaticity and surface area, rather than relying solely on surface area, enhances the degradation of alkanes. Additionally, biochar with a higher O/C ratio, indicating greater molecular polarity, facilitates the removal of aromatics, polar substances, and asphaltene [38]. Although biochar exhibits lower O/C and H/C ratios, the increased abundance of graphitic structures inside biochar enhances the rates of electron transport. However, the colonization of biochar by microorganisms can affect the kinetics and pathways of electron transfer. Studies have demonstrated that different types of biochar incorporated into soils can influence

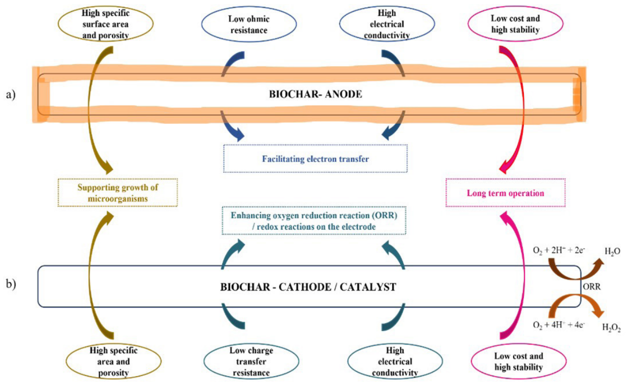

Figure 2: Functional considerations for biochar-based anodes **(a)** and cathodes/catalysts **(b)** in METs impacting bio-electrochemical performance.

biological processes by altering soil geochemical properties and increasing the metabolic carbon content [39]. A notable instance showcasing the impact of biochar on electron transfer in MET involves the utilization of corncob in conjunction with a glucose-feeding substrate. This combination led to an augmentation in the release of organic compounds towards the anodic side, consequently introducing a higher quantity of electrons into the circuit [4].

Wood-based biochars produced comparable power outputs to granular activated carbon and graphite granules. Wood-derived biochar also exhibited higher adsorption capacity and greater removal of chemical oxygen demand compared to granular activated carbon in a packed bed column study [40]. The addition of copper metal to activated carbon obtained from coconut shells resulted in improved performance of anode electrodes for the treatment of tannery effluent. Furthermore, a research investigation conducted on wetlands made with microbial fuel cells demonstrated that the use of corncob as a substrate led to enhanced efficiency in nitrogen removal and increased power generation capabilities [41]. Biochar, derived from biomass such as cotton stalks, has the potential to serve as a valuable nutrient reservoir for enhancing plant growth in soil subsequent to nutrient extraction from water sources. Additionally, it maintains biocatalysts and microbes in soil based METs, ensuring continuous power generation. This demonstrates the potential of biochar for sustainable nutrient recycling and energy production [4]. Table 1 provides an overview of different agriculture waste biochar, preparation process, composition of elements, and feeding substrate used in METs, including their electrochemical performances. The utilization of nano-graphene electrodes is prevalent in a diverse range of electrochemical gadgets owing to its remarkable electrical conductivity and expansive surface area. Biochar, a carbon-rich substance generated by the thermal decomposition of residual biomass, exhibits promise as a potential precursor for the synthesis of graphene-derived commodities. Through a series of chemical or thermal processes, biochar can be transformed into graphene or graphene oxide, which can then be used to fabricate nano-graphene electrodes. This approach can be considered an environmentally friendly way to utilize biowastes for electrode improvement [42]. In addition to nano-graphene electrodes, various other types of electrodes, such as carbon-based electrodes or metal-based electrodes, can also benefit from the incorporation of biowastes. When subjected to suitable processing and modification techniques, biowastes have the potential to augment the electrical conductivity, porosity, and surface area of such electrodes. For example, biochar or activated carbon derived from biowastes can be incorporated into the electrode structure to improve its electrochemical properties. In some cases, bioactive compounds from biowastes may also be used to functionalize electrode surfaces for specific bio electrochemical applications [43].

Cathodes and catalyst modifications

The ORR poses a significant obstacle in the advancement of METs, as it necessitates the utilization of electrocatalysts to enhance reaction rates and mitigate overpotential at the cathode (Figure 2b). Nevertheless, the practical implementation of METs faces obstacles due to the elevated expenses and toxic properties associated with catalysts like platinum and other metal-based alternatives [48]. As a solution to this challenge, scientists have explored alternative approaches, such as employing biochar derived from coconut shells, which exhibit a remarkable surface area of 1300 m^2/g, as an adsorbent. Notably, this biochar has demonstrated remarkable effectiveness in the removal of methylene blue, achieving an impressive removal rate of 98% in just 30 min [4]. When employing non-platinum catalysts in METs, it is advised to adhere to the 4-electron pathway for the direct reduction of oxygen to hydroxide ions [47]. Water hyacinth biochar, when used as a catalyst in METs or showed superior performance compared to commercially available catalysts. t achieved an improved power density of approximately 25 mW/m^2, outperforming Pt/C (12.3 mW/m^2), while preserving a transfer rate of 2.58 electrons [45]. Similarly, the utilization of banana biochar resulted in the transfer of 2.65 electrons per oxygen molecule and led to the generation of a power density of approximately 528 mW/m^2 [46]. The results of this study emphasize the potential of biochar as a highly efficient catalyst in METs, surpassing conventional commercially available alternatives. In addition, it is important to note that the elemental composition of the electrode has a crucial role in determining both the adherence of the electroactive biofilm and its electrocatalytic effective-

Table1: Analysis based on the performance of agriculture waste biochar.

Agriculture waste biochar	Preparation process		Element composition (%)				Electrode	Feeding substrate	Surface area (m^2/g)	Power density (mW/m^2)	Ref.
	Temperature	Residence time	C	O	H	N					
Coconut shells	Carbonization 500 °C	1 h at rate of 10 °C/min	51.1	43.1	5.6	0.1	Anode	Sewage sludge	0.2162	1069	[44]
Water hyacinth	Pyrolysis 900 °C	2 h with N_2 at rate 25 °C/min	-	-	-	-	Cathode/catalyst	Sucrose	25.924	24.47	[45]
Banana	Pyrolysis 900 °C	2 h with Ar gas	85.97	-	-	1.34	Cathode/catalyst	Sodium acetate	172.3	528.2	[46]
Coffee	Pyrolysis 400 - 600 °C	2 h in absence of O_2	45.4	47.1	3.2	3.4	Anode	Domestic waste	232	3927	[4]
Corncob	Pyrolysis 450 °C	2 h under N_2 gas	84.56	8.87	5.4	3.13	Cathode/catalyst	Sodium acetate	655.89	456.85 mW/m^3	[47]
Cotton stalks	Pyrolysis 450 °C	1 h under limited O_2	42.8	35	5.4	1.4	Anode	-	-	-550 mV (via 1000 Ω)	[4]

ness. Biomass-derived from plant sources, such as watermelon rind, exhibits a high concentration of C-N bonds and pyridinic nitrogen components. This biomass can be utilized as a viable feedstock for the synthesis of hierarchically structured carbon materials with porous properties. These carbon materials can serve as catalysts for the ORR [49]. The presence of pyridinic nitrogen facilitates the transfer of electrons to the conjugated pi bond, whereas graphitic nitrogen lowers the thermodynamic barrier of the ORR. By incorporating coconut shell powders, the carbon content is increased, leading to improved conductivity. The ORR serves as a reliable indicator of biochar stability in the fluid environment of METs, and achieving exceptional catalytic activity for ORR electrocatalysts necessitates the optimization of both mass transport and electron transfer processes [4].

Cathodes fabricated by biochar in METs face challenges like expansion, solvation, bleaching, clustering, moistening, and stripping, which can impact the performance of METs. Even though lotus leaves are not conventionally classified as agricultural waste, their distinctive properties render them promising contenders for biochar-based cathodes in METs. Lotus leaves exhibit exceptional water-repellent properties, a three-dimensional morphology, a proficient surface area for catalytic performance, and appropriate carbon, oxygen, and reactive nitrogen components [50]. This highlights the potential of utilizing natural agricultural waste for sustainable and cost-effective fabrication of electrocatalysts in METs.

Environmental and Economic Considerations of Agricultural Waste-derived Bioelectrodes

Agricultural waste-derived bioelectrodes offer several environmental and economic benefits, contributing to sustainable and cost-effective solutions [51]. The following are some key considerations in terms of their environmental and economic impact.

Environmental considerations

Waste reduction

By utilizing agricultural waste as a precursor for bioelectrodes, the burden on landfill sites is reduced. This approach aids in mitigating the environmental consequences of garbage accumulation and encourages the adoption of more sustainable waste management practices [52].

Renewable resource

Agricultural waste is a renewable resource that can be continuously generated from farming activities. By repurposing this waste for bioelectrode production, reduces the reliance on non-renewable resources, such as fossil fuels, and supports a more sustainable approach [53].

Carbon footprint reduction

Agricultural waste-derived bioelectrodes often have a lower carbon footprint compared to traditional electrode materials. By utilizing waste materials instead of fossil fuel-derived resources, greenhouse gas emissions associated with extraction and processing are reduced, contributing to climate change mitigation [52].

Economic considerations

Cost-effectiveness

Agricultural waste is generally available at a low or even no cost since it is a byproduct of agricultural processes. By employing this waste as a primary resource for bioelectrodes, there is a notable potential for a substantial reduction in production expenses, hence enhancing their economic feasibility [54].

Local resource utilization

Agricultural waste is often available locally, particularly in agricultural regions. By utilizing this local resource, transportation costs and logistics are minimized, promoting regional economic development, and supporting local industries.

Value-added products

Converting agricultural waste into bioelectrodes creates value-added products from materials that would otherwise be discarded. This opens new revenue streams and business opportunities, benefiting farmers and agricultural communities [53].

By considering these environmental and economic aspects, the utilization of agricultural waste-derived bioelectrodes presents a win-win scenario. It addresses environmental challenges by reducing waste and carbon emissions while offering economic benefits through cost-effective production and value creation from agricultural waste.

Conclusion

The utilization of agricultural waste as a valuable resource in the production of bioelectrodes for METs holds significant potential in terms of offering sustainable and economically feasible solutions. The present review has undertaken an examination of diverse facets pertaining to bioelectrodes obtained from agricultural waste. These facets encompass the categorization of agricultural waste employed as electrode materials, the transformation of agricultural waste into biochar, and the utilization of characterisation approaches to evaluate their efficacy. The review has highlighted that agricultural waste materials like cellulose, hemicellulose, and lignin can be efficiently employed to customize the characteristics of bioelectrodes and hybrid electrodes. The optimization of individual applications can be achieved by modifying the composition and ratios of the components, thereby enhancing the electrical conductivity, surface area, porosity, and mechanical strength of the electrodes. This modification facilitates the enhancement of electrode performance, stability, and efficiency of METs and other electrochemical applications. The prospect of utilizing agricultural waste as a viable supply for bioelectrodes is noteworthy in terms of sustainability, cost-effectiveness, and environmental conservation. By adopting these novel ideas, we may augment the efficacy, cost-effectiveness, and ecological soundness of

METs, thus facilitating the realization of a more sustainable future. Bioelectrodes made from agricultural waste are being studied and put to use in important ways that promote the idea of a circular economy and make the best possible use of renewable resources.

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Conflict of Interest

None.

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