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Lignocellulosic Bio Waste-Derived Bio-Graphite as a Green Anode Material in Lithium-Ion Batteries: A Review of Synthesis Methods.

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ABSTRACT
The growing demand for sustainable energy storage technologies has intensified the search into environmentally friendly and cost-effective materials for lithium-ion batteries (LIBs).). Graphite, the conventional anode material, faces challenges related to resource limitations and the environmental impact of synthetic production methods. As a promising alternative, lignocellulosic biomass-derived bio graphite offers a renewable, abundant and low-costs carbon source for anode applications. this review provides a comprehensive overview of current synthesis methods for converting lignocellulosic biomass into bio-graphite, with a focus on the structural, morphological and electrochemical characteristics of the resulting materials. Key synthesis routes discussed include pyrolysis, chemical activation, catalytic graphitisation, plasma-assisted and hydrothermal carbonisation highlighting the role of processing conditions and precursor composition in influencing graphite quality and performance. Special emphasis has been given to catalytic graphitization and hydrothermal carbonisation, which enable the formation of graphitic carbon at relatively low temperatures through the use of transition metal catalysts. Finally, the review identifies critical knowledge gaps and future directions needed to advance the use of lignocellulosic bio-waste in the scalable and sustainable production of high-performance LIB anodes.

Keywords: battery anode, bio-graphite, lignocellulosic bio waste, Lithium ion battery, synthesis methods

1. Introduction

The world's population is constantly growing, putting pressure on the already depleting fossil fuel-based energy systems (Usmani et al., 2020); (Gollakota, Kishore and Gu, 2018). This, together with the high levels of carbon emissions into the environment, has led to the increased exploitation of alternative renewable and greener sources of energy, such as wind and solar (Malyan et al., 2021); (Chen et al., 2020); (Liu, 2023). However, their intermittency, coupled with the requirement for stored energy in various applications, has necessitated the development of affordable, effective, and sustainable energy storage technologies.

1.1 Background on Li-ion batteries and the role of anode materials

The development of large-scale and nano-electronic devices, as well as electric cars, has made energy storage especially crucial (Sun et al., 2021); (Review, 2024); (Chen et al., 2020); (Chang et al., 2021). A wide range of energy storage technologies have been developed, including Li-polymer, Li-ion, and nickel metal hydride batteries. However, Li-ion batteries have dominated energy storage systems because of their long life cycle, high energy density, and stable operation (Goodenough and Park, 2013); (Xu et al., 2023); (Ahmed and Maraz, 2023). Despite the wide applicability of Li-ion batteries, more needs to be done to increase their efficiency. The advancement of anode materials is more critical than that of cathode materials in the creation of advanced lithium-ion battery electrodes (Review et al., 2023); (Ahmed and Maraz, 2023); (Chen et al., 2020). Natural graphite as an anode material, has a number of drawbacks, such as a low theoretical capacity and environmental issues related to its extraction and processing (Yap et al., 2023). Synthetic graphite production processes as well face problems such as extremely high energy intensity, unsustainability, and scaling up challenges. This has made the research into more sustainable and high-performance carbonaceous material derived from bio-waste as alternative for Li-ion batteries even more relevant. Graphite from agricultural bio-waste materials is a promising alternative to natural and synthetic graphite, yet more work is needed to address the challenges associated with its synthesis (Yap et al., 2023)

1.2 Limitations of conventional graphite

Graphite is a crystalline form of carbon consisting of a layered planar structure composed of carbon atoms that have undergone sp^2 hybridization. Each carbon atom is covalently bonded to three other carbon atoms in a hexagonal pattern to generate large two-dimensional graphene sheets. Slippage between layers is made possible by the weak van der Waals forces holding these sheets parallel to one another (Banek et al., 2018); (Li, Yamashita and Kita, 2021); (Jara et al., 2019). Owing to its excellent electrical conductivity, mechanical stability, and chemical inertness, graphite is widely used in energy storage, lubricants, refractories, and especially in the fabrication of lithium-ion battery anodes (Wu et al., 2019). Graphite exists in both natural and synthetic forms. However, the production of both natural and synthetic graphite faces serious challenges. Natural graphite is typically extracted through open-pit or underground mining, leading to substantial land degradation, deforestation, and loss of biodiversity. The flotation and purification stages of natural graphite often employ harsh chemicals such as hydrofluoric acid, which can result in water and soil contamination if not properly managed (Yap et al., 2023); (Liang et al., 2021); (Sanz et al., 2022); (Pusarapu et al., 2024).. Moreover, with China providing 66% of the world's natural graphite powders, the graphite supply chain has also become geopolitically concentrated, raising concerns about resource sustainability, market volatility, and ethical sourcing practices (European Carbon and Graphite Association, 2020). On the other hand, synthetic graphite, despite offering more uniform properties, is derived from non-renewable petroleum-based feed-stocks such as petroleum coke and coal tar pitch. Its production involves high-temperature graphitization processes often exceeding 2500 °C, which makes it extremely energy intensive and contributes significantly to greenhouse gas emissions. The synthesis methods may also produce hazardous by-products and rely on fossil fuel inputs, thereby intensifying their environmental footprint (Surovtseva et al., 2022); (Kulkarni et al., 2022). These challenges highlight the urgent need for more environmentally friendly and sustainable sources of graphite for energy storage applications.

1.3 The case for sustainable alternatives: bio-graphite from lignocellulosic waste

Lignocellulosic bio-waste has emerged as a promising sustainable and ideal cellulose based natural fiber

which can be used as an alternative to conventional graphite sources (Dungani et al,. 2018). Lignocellulosic bio-waste comprises agricultural residues such as nut shells, corn stalks, rice husks, sawdust, and bagasse, which are abundant and remain underutilized in many parts of the world (Kumar et al., 2021). Owing to the rapid depletion of non-renewable resources and increasing environmental pollution, there is a growing imperative to focus on utilizing these biological resources, leading to ongoing advancements and improvements in various utilization technologies (Singh et al, 2023). Utilizing such biomass for the production of bio-graphite not only offers a route to value addition but also contributes to waste management and circular economy objectives (Yuan et al., 2022). Lignocellulosic biomass is naturally porous with a hierarchical structure and large surface area (Tang et al., 2017). The porous structure is beneficial since it provides an ion transport path way and it can be easily combined with other materials to form a hybrid material that exhibits enhanced material electrochemical properties (Xiao et al., 2017) . Lignocellulosic bio waste is also a carbon rich material with heteroatom-doping characteristics, making it attractive for use as a substitute of conventional carbon material (Tang et al., 2017). Unlike synthetic graphite, bio-derived carbon materials can be produced at relatively lower temperatures and with minimal chemical additives, resulting in reduced energy consumption and a lower environmental impact (Sharma et al., 2020). Biomass is also considered carbon neutral because the carbon dioxide released during thermal decomposition is generally offset by that absorbed during plant growth (Sun & Liu, 2021). The diverse structure of lignocellulosic biomass allows for tunable carbon properties, such as porosity, surface area, and electrical conductivity, which are essential for effective lithium-ion battery anode performance (Ahmed et al. 2023). Additionally, the decentralized nature of biomass availability enables localized processing, which can reduce transportation-related emissions and stimulate rural economic growth (Gao et al., 2022). These advantages position lignocellulosic bio-waste as a viable and green precursor for sustainable anode materials, aligning with global efforts toward cleaner energy technologies and reduced dependence on fossil-based resources (UNEP, 2020).

1.4 Scope, Objectives and structure of the review

This review is centred on exploring the synthesis methods and the potential of lignocellulosic bio-waste as a sustainable precursor for producing bio-graphite, specifically for use as an anode material in Lithium ion batteries. With the growing global demand for Lithium ion batteries and rising concerns over the environmental and economic costs associated with natural and synthetic graphite, there is an urgent need to investigate renewable and low-environmental impact alternatives. This review aims to provide a comprehensive overview of the current techniques used to convert lignocellulosic biomass into high performance bio graphite, including thermal, chemical, catalytic and emerging synthesis routes. They key objectives are to: (i) examine the physicochemical properties of different lignocellusic feedstocks relevant to graphite production, (ii) analyse and compare the effectiveness and sustainability of various carbonization and graphitization processes, (iii) evaluate the structural and electro chemical characteristics of the resulting bio-graphite, and (iv) identify challenges, research gaps, and opportunities for scaling up production for practical energy storage applications. The structure of the review follows a logical progression, beginning with the fundamentals of lignocellulosic biomass and the role of graphite in lithium ion batteries, followed by a detailed analysis of the synthesis routes, characterisation techniques and comparative performance assessments. The review concludes with a discussion of environmental implications, current limitations, and future directions to guide further research and industrial applications.

2.0 Fundamentals of Lignocellulosic biomass and graphite

2.1. Chemical compositions of biomass and potential for graphite synthesis

Lignocellulosic biomass has a complex hierarchical structure which comprise of complex polymers and they include 35 – 50% cellulose $(C_6H_{10}O_5)n$, 20-35 % hemicellulose $(C_5H_8O_4)m$ and 10-30 % lignin $[C_9H_{10}O_3(OCH_3)(0.9\text{-}1.7)]n$ depending with specie (George et al., 2024). Cellulose is a liner polymer of glucose units which provides biomass with its fibrous strength. The hemicellulose is a branched polymer which is more thermally labile than cellulose. Lignin is a complex aromatic polymer, with a high carbon content and gives biomass its thermal stability (Demirbas, 2007). It is the high carbon content in lignin which is very crucial for bio char production. This is because lignin decomposes over a broader range of temperature, contributing to bio char yield. After thermal treatment, lignin yields more aromatic carbon, favouring graphitic structures, has low ash content thereby reducing impurities that hinder conductivity as well as naturally having a porous structure which enhance ion transport in electrochemical applications(Igalavithana et al., 2017); (Frohs and Jäger, 2021). The conversion of lignocellusic biomass materials to carbon materials can begin with carbonizing under inert conditions, followed by graphitising at temperature >2000 ℃ or at lower temperatures when the process is catalysed. Though lignocellulosic materials have a high potential, they face challenges such as high oxygen content and ash content, which both lead to poor electrical conductivity, low initial graphitic order and thus require high temperatures for graphitization, resulting in high costs. Additionally, the chemical composition of lignocellulosic may vary with species, growth conditions and their place (Kamal, Othman and Jabarullah, 2020).

The proximate, ultimate and lignin composition analysis of selected biomass waste shown in **Table 1** show that lignocellulosic bio waste material generally have high carbon content.

Table 1: Proximate and ultimate analysis(Yap et al., 2023)

Bio mass waste	Moisture Content	Ash Content	Volatile matter	C	H	N	O	S	Lignin (%)
Rice husks	9.40	13.20	62.00	37.80	4.73	0.45	43.50	0.17	20-25
Cotton stalk	NA	3.14	80.54	47.12	6.25	0.57	42.79	NA	20-25
Saw dust	NA	0.42	85.14	50.64	6.00	0.07	43.29	NA	
Macadamia nut shells	10.00	0.40	71.0	57.50	5.95	0.33	36.20	0.60	35-40
Chestnut shell	NA	0.00	73.23	46.68	5.94	0.62	46.76	NA	
Coconut shell	12.55	0.42	N/A	51.60	5.60	0.10	42.70	0.0	35-40

Thermochemical conversion processes such as pyrolysis can therefore be successfully done on this bio waste, producing bio char, which can be modified into carbon materials for use in energy storage applications (Xiao et al., 2017). Various lignocellulosic bio waste such as nut shells, rice husks, coconut shells have been studied for this purpose, demonstrating good porosity, surface area, and electrical performance when processed appropriately. Rice straw-derived bio chars were synthesized at various temperatures, that is 400, 550, 700, and 900 °C all exhibited reversible capacities though below 200 mAhg-

[1]. Li et al. 2020 reviewed biomass-derived carbon material for Li-ion batteries, reporting capacities ranging from 250-500 $mAhg^{-1}$ depending on the feedstock and the processing conditions (Li, Yamashita and Kita, 2021). This shows that biomass based carbon materials have the potential to be utilised for Li-ion battery anodes.

2.2. Graphite and its suitable properties for anode use

Graphite is a crystalline form of carbon which consists of a layered planar structure composed of carbon atoms that have undergone sp^2 hybridization (Frohs and Jäger, 2021). Each carbon atom is covalently bonded to three other carbon atoms in a hexagonal pattern to generate large two-dimensional graphene sheets The weak van der Waals forces holding these sheets parallel to one another enable slippage between layers (Banek et al., 2018); (Li, Yamashita and Kita, 2021); (Jara et al., 2019); (Gimåker and Granberg, 2021).

The performance of any electrode material depends to a greater extent on its structural organisation, degree of graphitisation and post treatment methods such as chemical activation or catalyst-assisted graphitization during its synthesis(Kane, Warnat and Ryan, 2021). This will determine the specific physical, chemical and electrochemical properties it must possess for anode application, which include high electrical conductivity, low porosity, and suitable lithium storage capacity(Qin et al., 2020); (Liu, 2023) These properties are obtained through characterisation to optimise their use (Igalavithana et al., 2017).

2.2.1 Surface area and pore structure

The surface area of bio graphite refers to the total available surface area of the material. In porous materials such as bio graphite, this includes both external and the internal surfaces within pores. The pore structure of the bio graphite refers to the size, distribution, shape and volume of pores in the material(Shi et al., 2023). The pores are named according to the size range, that is micro pores are less than 2 nm, mesoporous in the range of 2 – 50 nm and macro pores in the range greater than 50 nm.

Surface area and pore structure are very important features for anode material since they determine how well the bio graphite can interact with and store Li-ions during battery cycles. High surface area increase the number of active sites for Li-ion intercalation into the graphite. This enhances reaction kinetics, thereby contributing to higher power capability for the battery and also faster ion transport when contact with the electrolyte is improved. An optimized pore structure in the mesoporous region ensures provision of channel for ion transport, enhancing ion reversibility.

2.2.2 Crystallinity and degree of graphitization

In carbon materials, crystallinity refers to how well the carbon atoms are arranged in graphitic layers whereas degree of graphitization is a measure of how much the carbon materials resemble pure graphite in terms of structure (Kamal, Othman and Jabarullah, 2020). Crystallinity reflects the transformation of amorphous or disordered carbon into crystalline graphite during thermal treatment. The degree of graphitization is an important parameter for anode material since it determines how well Li-ions intercalate during the charging and de-intercalate during discharging, determining reversibility and efficiency(Li, Yamashita and Kita, 2021). crystalline graphite has a higher electrical conductivity and thus the electrode conductivity is improved, reducing internal resistance. Well-ordered graphite also has a high storage capacity, storing lithium ions with a theoretical capacity of up to 372 mAh/g as compared to amorphous carbon. More graphitised structure is chemically and mechanically stable and thus, Li-ion batteries have an excellent battery performance and a longer life cycle.

The crystallographic parameters for graphite, provided by an XRD include the (002) peak, which is approximately 26 ° (2θ), which represents the stacking of graphene layers along the c-axis. Sharper and stronger peaks represent higher crystallinity and better graphitization. The interlayer spacing (d_{002}) for graphite, is approximately 0.335 nm and 0.340-0.360 nm for disordered carbon (Zhang et al., 2022); (Gimåker and Granberg, 2021); (Shi et al., 2023)

2.2.3 Electrical Conductivity

The ease with which electrons can move through a substance in bio graphite is often influenced by the degree of graphitization. The more graphitic the structure, the better the conductivity. Electrical conductivity is also a critical property for bio graphite because the higher the conductivity, the easier it is for electrons to move through the anode to the external circuit, thus minimising resistance and energy loss. The bio-graphite produced from biomass-derived source exhibits exceptional electrical conductivity, reaching up to 3.58 x 10^4 S/m (Banek et al., 2018). This high conductivity is attributed to the sp^2 bonding in the graphite structure which facilitates efficient electron transfer and is crucial for battery applications (Kim et al., 2024). In bio-graphite, conductivity also helps indicate how successful the synthesis route has been in converting biomass to bio-graphite

3 Biomass-to-graphite synthesis routes

The preparation of bio graphite from biomass involves converting carbon-rich biomass into a graphitic form of carbon often, often intended for use in energy storage such as Li-ion batteries, catalysis or as adsorbents. Several routes exist and these include the traditional ones such as direct pyrolysis followed by graphitisation and chemical activation followed by thermal treatment. The novel and hybridized methods include catalytic graphitisation. Microwave-assisted graphitisation hydrothermal carbonization plus catalytic treatment and also template assisted synthesis. each synthesis route has its own distinct advantages and disadvantages depending on the biomass type, desired graphite quality and end-use. A detailed account of some of the synthesis routes has been given.

3.1. Direct Pyrolysis + graphitization

This traditional synthesis method of graphite from biomass generally involves two steps of heat treatment, carbonization(pyrolysis) and graphitization. Biomass is first carbonized via the pyrolysis process to produce bio char. Pyrolysis is the commonest carbonisation method because of its simplicity and the ability to produce high quality carbon material.

3.1.1. Pyrolysis

Pyrolysis is a thermochemical process where organic materials is decomposed at high temperatures in the absence of oxygen typically between 300 and 600 ºC. (Sharma, Pareek and Zhang, 2015) ; (Khuenkaeo and Tippayawong 2020) . The thermal decomposition of biomass in a pyrolysis reactor is affected by several conditions which include temperature, heating rate, residence time, feed particle size, reaction time, feed composition and also feed rate (Hasan, Rasul and Khan, 2022). For the production of char, slow pyrolysis is normally employed. Different types of materials are used as feedstock for the process and they range from agricultural residues, forestry residues, municipal solid waste, algae and manure (Adelawon et al., 2021). Lignocellusic are known to have high carbon yield and they produce high quality bio char. The pyrolysis process mainly take place in a pyrolysis reactor and it can have different configurations depending on the applications, the feedstock, the temperatures to be reached.

3.1.2 Graphitization

After the pyrolysis stage, the process is followed by graphitization, which is the process by which carbon materials are transformed into graphite, which is the crystalline form of carbon where atoms are arranged in a hexagonal lattice structure (Panda et al., 2018). This process involves both structural and chemical changes, converting amorphous carbon into ordered and stacked graphene layers. The layers of the carbon atoms will align parallel and interlayer spacing decreases to the value of characteristic graphite. As the graphitisation process progresses, the stacking height and the in-plane size increases. The defects in the structure decrease, improving electrical conductivity, thermal stability and mechanical strength. The process occurs at very high temperatures, typically in the range of 2000 – 3000 ºC or even more. When exposed to such temperatures, carbonaceous materials such bio char is converted into graphite.

The direct pyrolysis and graphitization method for converting lignocellulosic biomass into bio-graphite offers relatively simple and sustainable pathway. However, the method is heat intensive, making it costly. If complete graphitization is to be achieved, char is treated to a temperature of about 2500 ºC or more for a period of over 24 hours (Shi and Ziyi, 2021), (He, Shang and Tan, 2024). This comes after the pyrolysis process, which requires its own fair share of energy, requiring temperatures in the ranges of up to 900 ºC (Wang et al., 2020). Additionally, there are challenges of incomplete graphitization at moderate temperatures and difficulties in maintaining consistency due to biomass heterogeneity (Chen et al., 2020). Environmentally, volatile organic compounds are released into the environment especially when fossil fuels are used for heating (Singh & Sharma, 2022). This calls for the integration of renewable heat energy sources as well as entailing the use of catalysts to lower the energy requirements of the process.

3.2. Chemical activation + thermal treatment

The chemical activation method involves mixing an activator and biomass materials evenly in a certain biomass constituent ratio, followed by slow pyrolysis under inert gas environment (Illingworth, Rand and Williams, 2022). The process involves impregnation of the raw biomass material with a chemical activating agent such as zinc chloride, phosphoric acid, potassium hydroxide, potassium carbonate or sodium hydroxide followed by carbonisation at temperatures typically between 400 and 800 ºC (Illingworth, Rand and Williams, 2022). Alternatively, a two-step process is used for chemical activation. This is where the biomass material is firstly pyrolysed to produce bio char followed by impregnation of the char with the chemical activation agent. The impregnated char is activated at high temperature to produce the activated carbon (Anto et al., 2021). The chemical activation method based on the potassium hydroxide activator is the most commonly used method to prepare bio graphite(Illingworth, Rand and Williams, 2022). The activation mechanism of KOH on carbon involves three main steps:

a. The chemical activation procedure employed to etch the carbon framework occurs through an oxidation-reduction reaction between carbon and potassium oxide, as shown in reactions (1)-(3). Potassium intercalates into the carbon matrix, resulting in structural expansion and thereby yielding a well-developed porous structure.
b. The physical activation process: The H_2O produced by reaction 4 and the CO_2 generated from reactions (5) and (6) within the activation system all contribute to the etching of carbon, which positively influences the enhanced development of the porosity of the carbon framework.
c. As illustrated in reactions (1), (7), and (2), the metallic potassium generated in the reaction can be efficiently incorporated into the carbon lattice, thereby inducing lattice expansion. Upon the removal of the inserted metallic potassium and potassium-based compounds through washing, the porous

structure of the carbon will experience further enlargement. The carbon activation process utilizing KOH encompasses chemical interactions, physical actions, and the lattice expansion of carbon induced by the insertion of metallic potassium into the carbon lattice.

$K_2O + C \rightarrow 2K + CO$ 1

$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3$ 2

$K_2CO_3 + 2C \rightarrow 2K + 3CO$ 3

$2KOH \rightarrow K_2O + H_2O$ 4

$CO + H_2O \rightarrow CO_2 + H_2$ 5

$K_2CO_3 \rightarrow K_2O + CO_2$ 6

$K_2 + H_2 \rightarrow 2K + H_2O$ 7

Chemical activation has the advantages of producing high surface area and porous carbon, which enhance electrochemical performance as well as lowering temperature below that of conventional graphite, thereby reducing energy demand. However, the major drawbacks of chemical activation are that it produces more of amorphous carbon rather than crystalline graphite and also its impact onto the environment because of its alkali nature. Thus there is need careful handling and for post treatment washing to reduce potential harm to life and equipment degradation. Large scale operations should consider effective wastewater treatment to reduce impact onto the environment. Research is also exploring greener activating agents to improve sustainability and environmental harm. Catalysis of the process using metal catalyst ensures the production of crystalline carbon. as well

3.3.Plasma-assisted graphitization

Plasma assisted graphitisation is a transformative process that enhances the conversion of carbon based materials into high quality graphitic structures. The process begins with plasma generation where an inert or reactive gas such as argon or nitrogen is ionised using a power source such microwave or direct current. This is followed by exposing the prepared biomass into the plasma field where it undergoes rapid heating at temperatures in the excess of 4000 ºC. thereby facilitating the breakdown of non-carbon elements and promoting the rearrangement of carbon atoms into graphitic structures (Purawiardi et al., 2024). The resultant graphitized material is then cooled under controlled conditions to prevent oxidation. In a typical plasma-assisted graphitization set-up, the heat was applied to pyrolysis the wood biomass sample in a pyrolysis chamber. The measured heat temperature was 4000 ºC (Purawiardi et al., 2024). The produced graphite was of high quality.

Plasma assisted graphite has several advantages compared to the traditional methods. The method produces superior graphene quality exhibiting high surface area and electrical conductivity due to better control over the graphitization process (Zhan et al., 2016). The process is ultrafast since plasma assisted electrochemical exfoliation allows for the quick generation of graphene sheets (Thanh et al., 2014). The challenges with synthesis route is that precise optimization of the plasma parameters such as gas type, power and exposure time are required (Zafar and Jacob, 2022); (Sun et al., 2021). Moreover, the setting up, the maintenance coupled with the energy intensive operation of the plasma systems are costly. The other big challenge is with the extreme temperatures involved, which require specialised materials such as ceramics and quartz for plasma containment. Large scale operation of plasma systems is also problematic because of the need to maintain uniform plasma treatment over large volumes (Samal, 2017). However, with ongoing research into hybrid plasma-catalytic systems, microwave-plasma coupling and integration with machine learning for process optimization, plasma assisted conversion could become a

clean and high performance route to synthesize bio graphite for the next generation of Li-ion batteries (Wang et al., 2022.

3.4.Catalytic Graphitization

Catalytic graphitization is a chemical reaction between a carbonaceous material and a catalyst to form graphite materials. This process utilises transition metal catalysts such as nickel, iron and cobalt to facilitate graphitization at lower temperatures compared to traditional methods, which typically require high energy inputs and non-renewable carbon sources. Research have shown that heat treatment of the carbon materials with a catalyst enhances the carbon crystallinity, further improving the efficiency of the overall graphitization process (Yap et al., 2023); .(Shi et al., 2023)

The kinetic mechanism of the process shows that with the help of catalyst, graphitization can be achieved at a minimum temperature of 600 ^{0}C (He, Shang and Tan, 2024). Catalytic graphitization of saw dust mixed with Fe or Ni catalysts have been reported at a temperature of 1000 °C resulting in nano sized graphitic structures of high crystallinity (Sevilla, 2007). A straightforward one-step process comprising pyrolysis at 1200 °C was also employed to graphitize a range of biomass feed stocks, including softwood, hardwood, cellulose, glucose, organosolv lignin, and hydrolysis lignin, utilizing an inexpensive, earth-abundant iron catalyst (Sagues et al., 2020); (Lower et al., 2023). The lowering of graphitization temperature requirements significantly reduces energy costs of the process (Nuriskasari, Zulfia Syahrial and Wahyuadi M Soedarsono, 2023); (Pusarapu et al., 2024).

Catalytic graphitisation can be a single step where biomass is catalyst impregnated followed by heat treatment or a two-step process that involves carbonisation of biomass first, impregnation then graphitisation (Kamal, Othman and Jabarullah, 2020). The use of catalysts improves the graphitization degree of carbon materials (Yang et al., 2023). The physicochemical properties of the resulting graphite such as crystallite size and structural order are greatly improved, making it comparable to commercial graphite(Hunter, Ramírez-Rico and Schnepp, 2022)

Catalytic graphitization is one of the most promising and energy efficient methods for converting lignocellulosic biomass into bio graphite, especially for electrochemical applications such as Li-ion batteries. It produces graphitic carbon with a good crystallinity, improved conductivity and suitable interlayer spacing for lithium interaction. The process is also scalable and can be adapted to various types of biomass, converting low-value lignocellulosic biomass into high performance and sustainable materials (Liu, 2023). However, it presence challenges such as the need for precise control of catalyst loading and distribution for uniform graphitization to avoid residual metal particles remaining in the final product, potentially affecting purity and stability. In addition, post-treatment steps such as acid washing are often required to remove metal residues, which may increase chemical usage and wastewater production. From an environmental perspective, while the method reduces energy input, improper disposal of spent catalysts or leachates can pose ecological risks if not managed properly. Looking ahead, the development of recyclable, low-toxicity catalysts, as well as single-step graphitization techniques, is a key research focus. Furthermore, coupling catalytic graphitization with machine learning optimization, green solvents, or renewable heat sources can improve.

3.5.Hydrothermal carbonisation + catalytic treatment (HTC)

HTC is a two-step synthesis route for the conversion of biomass into bio graphite. Initially the biomass is subjected to hydrothermal carbonisation where it is treated with water at elevated temperatures, typically of 180-250 °C in an enclosed system. This process breaks down lignocellulosic structures, producing hydro char. Secondly, the hydro char undergoes catalytic graphitisation, where it is mixed with transitional

metal catalysts such as iron, cobalt or nickel and heated at moderate temperatures of about 800-1000 ºC under an inert environment. The metal catalysts facilitate the re-arrangement of disordered carbon structure in hydro char into more ordered graphitic domains through a dissolution-precipitation mechanism, resulting in bio graphite with enhanced conductivity, structural order and desirable surface properties for anode applications (Gimåker and Granberg, 2021).

HTC method provides a promising route for valorising biomass into high value carbon materials, offering several advantages than the conventional thermal processes. Being able to process wet biomass, the method eliminates the need for biomass drying. When metal catalysts are employed as well, the conversion of amorphous carbon into graphitic carbon takes place at lower temperature compared to traditional graphitization. Both features of the process lower the energy requirements for the process. The process however faces challenges such as high cost and potential environmental risk of metal catalysts, difficulties in recovery and scalability issues. Environmentally, the wastewater generated, volatile emissions during catalytic treatment are a cause for concern. Despite these drawbacks, the method holds strong future potential: integrating it with renewable energy sources could improve sustainability, while advances in recyclable or bio-based catalysts may lower environmental impacts.

Conclusion

The transformation of lignocellulosic bio-waste into bio graphite presents a sustainable and environmentally friendly alternative to conventionally graphite for lithium-ion batteries anodes. This review has examined the major synthesis methods such as pyrolysis, hydrothermal chemical activation, catalytic graphitisation, plasma- and hydrothermal carbonisation. In as much as the optimal approach for the transformation of lignocellulosic biomass waste into bio graphite is dependent upon specific applications, it is imperative to establish an equilibrium between the quality and the production costs. A route that concurrently yields high-quality bio graphite while ensuring high energy efficiency and reduced production costs would be exceedingly advantageous. In light of these considerations, catalytic graphitization and hydrothermal carbonization coupled with catalysis emerge as the most effective methodologies. Catalytic graphitization represents one of the techniques that can be employed to attain graphite characteristics utilizing minimal energy. Numerous scholars have successfully converted various forms of lignocellulosic biomass with the assistance of catalysts such as iron, cobalt, and nickel, thereby producing high-quality bio graphite particularly suited for electrochemical applications at moderate temperatures, resulting in superior energy efficiency in comparison to conventional thermal methods. Similarly, HTC coupled with metal catalysis has been reported to achieve high crystallinity and layered structures using low temperatures thereby consuming lower energy than methods like plasma and other high temperature routes. HTC is also ideal for wet biomass, making it very cost effective. Additionally, two methods, catalytic graphitisation and HTC have reasonable start-up costs and can be scaled-up more easily compared to other methods such as plasma. The incorporation of metal catalysts additionally contributes to the enhancement of electrical conductivity, a characteristic that is critically important for bio graphite intended to be used as anode material in Li-ion batteries. The major challenge associated with the two methods is the need for precise control over the catalysts loading and its removal in the product bio graphite yet the methods present a good opportunity for utilisation in the conversion of biomass waste to bio graphite.

Future perspectives across all biomass to bio graphite conversion routes therefore are centred on improving quality, sustainability and efficiency. The required thrust is the development of advanced

graphitisation technologies such as plasma enhanced method but with a much lower operating and start-up costs. Interest should also be focused on the development of low cost and environmentally friendly catalysts, including bio-based, metal free and recyclable ones to replace the traditional transitional metals, thereby reducing the environmental impact and production costs.

References

1. Adelawon, B.O. et al. (2021) 'Comparison of the slow , fast , and flash pyrolysis of recycled maize-cob biomass waste , box-benhken process optimization and characterization studies for the thermal fast pyrolysis production of bio- energy', Chemical Engineering Communications, 0(0), pp. 1–31. Available at: https://doi.org/10.1080/00986445.2021.1957851.
2. Ahmed, M.D. and Maraz, K.M. (2023) 'Revolutionizing energy storage: Overcoming challenges and unleashing the potential of next generation Lithium-ion battery technology', Materials Engineering Research, 5(1), pp. 265–278. Available at: https://doi.org/10.25082/mer.2023.01.003.
3. Anto, S. et al. (2021) 'Activation strategies for biochar to use as an efficient catalyst in various applications', Fuel, 285, p. 119205. Available at: https://doi.org/https://doi.org/10.1016/j.fuel.2020.119205.
4. Banek, N.A. et al. (2018) 'Sustainable Conversion of Lignocellulose to High-Purity, Highly Crystalline Flake Potato Graphite', ACS Sustainable Chemistry and Engineering, 6(10), pp. 13199–13207. Available at: https://doi.org/10.1021/acssuschemeng.8b02799.
5. Chang, H. et al. (2021) 'Recent developments in advanced anode materials for lithium-ion batteries'. Available at: https://doi.org/10.20517/energymater.2021.02.
6. Chen, Q. et al. (2020) 'Biomass-derived porous graphitic carbon materials for energy and environmental applications', Journal of Materials Chemistry A, 8(12), pp. 5773–5811. Available at: https://doi.org/10.1039/c9ta11618d.
7. Dungani, R., Aditiawati, P., Aprilia, S., Yuniarti, K., Karliati, T., Suwandhi, I. and Sumardi, I., 2018. Biomaterial from oil palm waste: properties, characterization and applications. Palm Oil, 31, pp.1-6.
8. European Carbon and Graphite Association (2020) 'Towards CO 2 neutrality due to carbon and graphite', Ecga [Preprint].
9. Frohs, W. and Jäger, H. (2021) 'The Element Carbon', Industrial Carbon and Graphite Materials: Raw Materials, Production and Applications: Volume 1 and 2, 1–2, pp. 21–31. Available at: https://doi.org/10.1002/9783527674046.ch2.
10. George, J. et al. (2024) 'Chemical Composition of Biomass', in S. Thomas et al. (eds) Handbook of Biomass. Singapore: Springer Nature Singapore, pp. 305–329. Available at: https://doi.org/10.1007/978-981-99-6727-8_10.
11. Gimåker, M. and Granberg, H. (2021) Graphite materials –Production from biomass? Available at: https://urn.kb.se/resolve?urn=urn:nbn:se:ri:diva-58964.
12. Gollakota, A.R.K., Kishore, N. and Gu, S. (2018) 'A review on hydrothermal liquefaction of biomass', Renewable and Sustainable Energy Reviews, 81(June 2017), pp. 1378–1392. Available at: https://doi.org/10.1016/j.rser.2017.05.178.
13. Goodenough, J.B. and Park, K.S. (2013) 'The Li-ion rechargeable battery: A perspective', Journal of the American Chemical Society, 135(4), pp. 1167–1176. Available at: https://doi.org/10.1021/ja3091438.
14. Hasan, M.M., Rasul, M.G. and Khan, M.M.K. (2022) 'The Effects of Slow and Fast Pyrolysis on the

Yields and Properties of Produced Bio-oils from Macadamia Nutshell', AIP Conference Proceedings, 2681. Available at: https://doi.org/10.1063/5.0114965.

15. He, Y., Shang, W. and Tan, P. (2024) 'Insight into rechargeable batteries under extreme pressure and gravity for deep space exploration', J. Mater. Chem. A, 12(40), pp. 27123–27129. Available at: https://doi.org/10.1039/D4TA04410J.
16. Hunter, R.D., Ramírez-Rico, J. and Schnepp, Z. (2022) 'Iron-catalyzed graphitization for the synthesis of nanostructured graphitic carbons', Journal of Materials Chemistry A, 10(9), pp. 4489–4516. Available at: https://doi.org/10.1039/d1ta09654k.
17. Igalavithana, A.D. et al. (2017) 'Advances and future directions of biochar characterization methods and applications', Critical Reviews in Environmental Science and Technology, 47(23), pp. 2275–2330. Available at: https://doi.org/10.1080/10643389.2017.1421844.
18. Illingworth, J.M., Rand, B. and Williams, P.T. (2022) 'Understanding the mechanism of two-step, pyrolysis-alkali chemical activation of fibrous biomass for the production of activated carbon fibre matting', Fuel Processing Technology, 235, p. 107348. Available at: https://doi.org/https://doi.org/10.1016/j.fuproc.2022.107348.
19. Jara, A.D. et al. (2019) 'Purification, application and current market trend of natural graphite: A review', International Journal of Mining Science and Technology, 29(5), pp. 671–689. Available at: https://doi.org/https://doi.org/10.1016/j.ijmst.2019.04.003.
20. Kamal, A.S., Othman, R. and Jabarullah, N.H. (2020) 'Preparation and synthesis of synthetic graphite from biomass waste: A review', Systematic Reviews in Pharmacy, 11(2), pp. 881–894.
21. Kane, S., Warnat, S. and Ryan, C. (2021) 'Improvements in methods for measuring the volume conductivity of electrically conductive carbon powders', Advanced Powder Technology, 32(3), pp. 702–709. Available at: https://doi.org/https://doi.org/10.1016/j.apt.2021.01.016.
22. Kim, Y. et al. (2024) 'Comparative study on the rheological properties of natural and synthetic graphite-based anode slurries for lithium-ion batteries', Korea-Australia Rheology Journal, 36(1), pp. 25–32. Available at: https://doi.org/10.1007/s13367-023-00079-6.
23. Kulkarni, S. et al. (2022) 'Prospective Life Cycle Assessment of Synthetic Graphite Manufactured via Electrochemical Graphitization', ACS Sustainable Chemistry \& Engineering, 10(41), pp. 13607–13618. Available at: https://doi.org/10.1021/acssuschemeng.2c02937.
24. Li, R., Yamashita, S. and Kita, H. (2021) 'Investigating the chemical bonding state of graphite powder treated with magnesium(II) phosphate through EELS, TEM, and XPS analysis', Diamond and Related Materials, 116, p. 108423. Available at: https://doi.org/https://doi.org/10.1016/j.diamond.2021.108423.
25. Liang, C. et al. (2021) 'Green synthesis of graphite from CO2 without graphitization process of amorphous carbon', Nature Communications, 12(1), pp. 1–9. Available at: https://doi.org/10.1038/s41467-020-20380-0.
26. Liu, Z. (2023) 'E ff ects of crystal structure and electronic properties on lithium storage performance of arti fi cial graphite', pp. 29923–29930. Available at: https://doi.org/10.1039/d3ra05785b.
27. Lower, L. et al. (2023) 'Catalytic Graphitization of Biocarbon for Lithium-Ion Anodes: A Minireview', ChemSusChem, 16(24). Available at: https://doi.org/10.1002/cssc.202300729.
28. Malyan, S.K. et al. (2021) 'Biochar for environmental sustainability in the energy-water-agroecosystem nexus', Renewable and Sustainable Energy Reviews, 149(June), p. 111379. Available at: https://doi.org/10.1016/j.rser.2021.111379.

29. Nuriskasari, I., Zulfia Syahrial, A. and Wahyuadi M Soedarsono, J. (2023) 'Catalytic Graphitization of Biomass as a Potential Method Produce Graphite In The Future : A Review', Recent in Engineering Science and Technology, 1(02), pp. 34–43. Available at: https://doi.org/10.59511/riestech.v1i02.17.
30. Purawiardi, I. et al. (2024) 'Numerical Analysis for Predicting the Rate of Graphitization on Wood Biomass during the Plasma-Assisted Pyrolysis', IOP Conference Series: Earth and Environmental Science, 1354(1). Available at: https://doi.org/10.1088/1755-1315/1354/1/012017.
31. Pusarapu, V. et al. (2024) 'Sustainable co-production of porous graphitic carbon and synthesis gas from biomass resources', npj Materials Sustainability, 2(1), pp. 1–10. Available at: https://doi.org/10.1038/s44296-024-00020-0.
32. Qin, C. et al. (2020) 'Understanding structure-performance correlation of biochar materials in environmental remediation and electrochemical devices', Chemical Engineering Journal, 382(July), p. 122977. Available at: https://doi.org/10.1016/j.cej.2019.122977.
33. Review, A. et al. (2023) 'Emerging and Recycling of Li-Ion Batteries to Aid in Energy Storage, A Review', Recycling, 8(48). Available at: https://doi.org/10.3390/recycling8030048.
34. Sagues, W.J. et al. (2020) 'A simple method for producing bio-based anode materials for lithium-ion batteries', Green Chemistry, 22(20), pp. 7093–7108. Available at: https://doi.org/10.1039/d0gc02286a.
35. Samal, S. (2017) 'Thermal plasma technology: The prospective future in material processing', Journal of Cleaner Production, 142, pp. 3131–3150. Available at: https://doi.org/10.1016/j.jclepro.2016.10.154.
36. Sanz, J. et al. (2022) 'Carbon (C) [Z{\thinspace}={\thinspace}6] (Graphite)', in Elements and Mineral Resources. Cham: Springer Nature Switzerland, pp. 59–62. Available at: https://doi.org/10.1007/978-3-030-85889-6_14.
37. Sharma, A., Pareek, V. and Zhang, D. (2015) 'Biomass pyrolysis - A review of modelling, process parameters and catalytic studies', Renewable and Sustainable Energy Reviews, 50, pp. 1081–1096. Available at: https://doi.org/10.1016/j.rser.2015.04.193.
38. Shi, Z. et al. (2023) 'Establishment of green graphite industry: Graphite from biomass and its various applications', SusMat, 3(3), pp. 402–415. Available at: https://doi.org/10.1002/sus2.139.
39. Shi and Ziyi (2021) 'Iron-catalyzed graphitization of biochar to produce graphitic carbon materials', pp. 13–19.
40. Sun, X. et al. (2021) 'Advance in Using Plasma Technology for Modification or Fabrication of Carbon-Based Materials and Their Applications in Environmental, Material, and Energy Fields', Advanced Functional Materials, 31(7), pp. 1–26. Available at: https://doi.org/10.1002/adfm.202006287.
41. Surovtseva, D. et al. (2022) 'Toward a life cycle inventory for graphite production', Journal of Industrial Ecology, 26(3), pp. 964–979. Available at: https://doi.org/https://doi.org/10.1111/jiec.13234.
42. Tang, W. et al. (2017) 'Natural biomass-derived carbons for electrochemical energy storage', Materials Research Bulletin, 88, pp. 234–241. Available at: https://doi.org/https://doi.org/10.1016/j.materresbull.2016.12.025.
43. Usmani, Z. et al. (2020) 'Advancement in valorization technologies to improve utilization of bio-based waste in bioeconomy context', Renewable and Sustainable Energy Reviews, 131(February), p. 109965. Available at: https://doi.org/10.1016/j.rser.2020.109965.

44. Wu, J. et al. (2019) 'The critical role of carbon in marrying silicon and graphite anodes for high-energy lithium-ion batteries', Carbon Energy, 1(1), pp. 57–76. Available at: https://doi.org/10.1002/cey2.2.
45. Xiao, P.-W. et al. (2017) 'Biomass-derived flexible porous carbon materials and their applications in supercapacitor and gas adsorption', Materials & Design, 129, pp. 164–172. Available at: https://doi.org/https://doi.org/10.1016/j.matdes.2017.05.035.
46. Xu, J. et al. (2023) 'High-Energy Lithium-Ion Batteries: Recent Progress and a Promising Future in Applications', Energy and Environmental Materials, 6(5), pp. 1–26. Available at: https://doi.org/10.1002/eem2.12450.
47. Yang, P. et al. (2023) 'Progress in the graphitization and applications of modified resin carbons', New Carbon Materials, 38(1), pp. 96–108. Available at: https://doi.org/https://doi.org/10.1016/S1872-5805(23)60715-2.
48. Yap, Y.W. et al. (2023) 'Recent Advances in Synthesis of Graphite from Agricultural Bio-Waste Material: A Review', Materials, 16(9), pp. 1–26. Available at: https://doi.org/10.3390/ma16093601.
49. Zafar, M.A. and Jacob, M. V. (2022) Plasma-based synthesis of graphene and applications: a focused review, Reviews of Modern Plasma Physics. Springer Nature Singapore. Available at: https://doi.org/10.1007/s41614-022-00102-3.
50. Zhang, L. et al. (2022) 'Microstructure graphitization evolution and multi-scale, multi-mechanism synergistic enhancement of ultra-high strength carbon-graphite materials', Diamond and Related Materials, 128, p. 109271. Available at: https://doi.org/https://doi.org/10.1016/j.diamond.2022.109271.