




Review

The Green Synthesis of Nanostructured Silicon Carbides (SiCs) from Sugarcane Bagasse Ash (SCBA) as Anodes in Lithium-Ion (Li-Ion) Batteries: A Review Paper

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Abstract: Silicon is a promising anode material for the increased performance of lithium-ion batteries because of its high elemental composition and specific capacity. The application of silicon on a commercial scale is restricted due to the limitation of volume expansion. Silicon is also expensive, making it difficult for large-scale commercialisation. Different methods were used to address these issues, including a sintering process and the sol-gel method, to form silicon carbide (SiC), a hard chemical compound containing silicon and carbon. The silicon carbide anode not only acts as a buffer for volume expansion but also allows for better infiltration of the electrolyte, increasing charge and discharge capacity in the battery. Like silicon, silicon carbides can be costly. The development of renewable energy systems is very important, especially in the development of energy storage systems that are not only efficient but also cost-friendly. The cost of the energy storage devices is lowered, making them easily accessible. Silicon carbides can be synthesised from sugarcane, which is the fibrous waste that remains after juice extraction. This could be beneficial, as we could never run out of such a resource, and it offers low carbon with a high surface area. Silicon carbides can be synthesised by carbothermal reduction of silica from sugarcane bagasse. This review provides a comprehensive understanding of silicon carbides and synthetic processes. The innovative use of waste to synthesise materials would reduce costs and comply with Sustainable Development Goals (SDGs) 7 (affordable and clean energy) and 13 (climate action).

Keywords: silicon waste; biochar; activation; lithium-ion batteries; energy storage systems; silicon carbides; silicon



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1. Introduction

There is growing concern about environmental changes and global warming due to the release of greenhouse gases from the continued use of fossil fuels [1]. The energy storage systems that we rely on are expensive to synthesise, making them very unaffordable. Renewable forms of energy are abundant, sustainable, reliable, and readily available. Since the 1950s, lithium has been an interesting material due to its high energy capacity [2]. When they entered the market, lithium-ion batteries (LIBs) developed and progressed rapidly, from their application and development in new energy in the electrical vehicle industry. Initially, for the cathode material, compounds such as manganese dioxide (MnO₂) and iron disulphide (FeS₂) were used, but lithium precipitates on the surface of the anode, forming dendrites and eventually breaking through the cell diaphragm, which in turn can result in a short-circuit explosion [3,4]. Ever since the concern about phone explosions, research has turned to anode materials.

Electrochemical energy storage systems (ESSs) like batteries are storage devices which store a lot of energy, and this is complemented by the power densities they possess. This can be seen in Table 1, which shows several batteries.

Table 1. Comparison of energy densities for different energy storage systems.

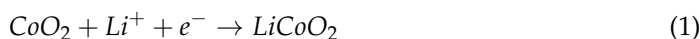
Energy Storage System (ESS)	Cycle Life	Energy Density (W·kg ⁻¹)	Energy Efficiency (%)
Lithium-ion batteries (LIBs)	4000–5000 [5]	110–160 [6]	85–90 [7]
Pb acid battery	500–1000 [5]	33 [8]	75–80 [8]
Ni-Cd battery	1500 [6]	45–80 [6]	78–85 [6]
Na-S battery	300 [9]	110.6 [9]	80–90 [7]

Table 1 shows that LIBs have improved power density, energy density, and energy efficiency compared to other batteries, such as nickel cadmium (Ni-Cd) or sodium sulphide (Na-S) [7]. Compared to lead (Pb) acid and nickel–metal hydride batteries, lithium-ion batteries (LIBs) are more promising energy storage devices because of their low discharge rates and the speed and efficiency of their performance. Furthermore, they can deliver the same or a greater level of energy at half the size and weight, unlike Pb-acid batteries, as they do not charge in stages. Furthermore, temperature fluctuations and energy depletion do not affect the overall power output of LIBs [10,11]. To satisfy the demand for ESSs, it is essential to develop materials with high electrochemical performance that are cost-friendly and do not contribute to the ongoing global climate crisis [12].

LIBs have high efficiency and excellent performance, along with additional characteristics, such as being lightweight and having a high storage capacity. Lithium-ion batteries are secondary batteries, signifying that they are rechargeable and that the overall reaction can be reversed. There is an increasing demand for long-lasting reliable energy systems [13]. LIBs have also become the leading ESSs in electrical vehicles due to their high energy density and high power density, as well as their long life [10]. LIBs transmute chemical energy into electrical energy; the operating voltage of LIBs is 1.5 V to 4.2 V [14]. Several cells must be placed in series to obtain direct voltage and capacity. There is a positive terminal, called the cathode, where the charge occurs, and a negative terminal, called the anode, where oxidation occurs when the cathode is discharged [15,16]. Both the anode and the cathode are soaked in the electrolyte, with a separator included to separate them [17,18].

The overall functionality of lithium-ion batteries can be improved by improving the cyclability of the anode and their higher rate capabilities. There are several solutions to meet the demands of long useful life, good overall power, and energy densities. For example, nanostructured materials, such as anodes, and better cathode capacity can improve electrode performance, improving overall efficiency [19].

The half-reaction:

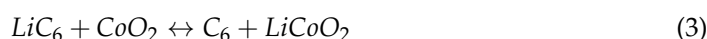


Oxidation occurs at the anode where the graphite compound is LiC_6 , which forms graphite and lithium ions.

The half-reaction:



The overall reaction:



The forward reaction represents discharge, and the reverse reaction represents charge, as shown in Equation (1). During charging, the lithium ions emitted from the cathode are delivered to the anode, and, during discharge, the lithium ions move back to the cathode, as represented in Figure 1. For a battery to be more efficient, the main focus should be

the electrolyte and the anode [20]. Therefore, it is important that they complement each other [21,22].

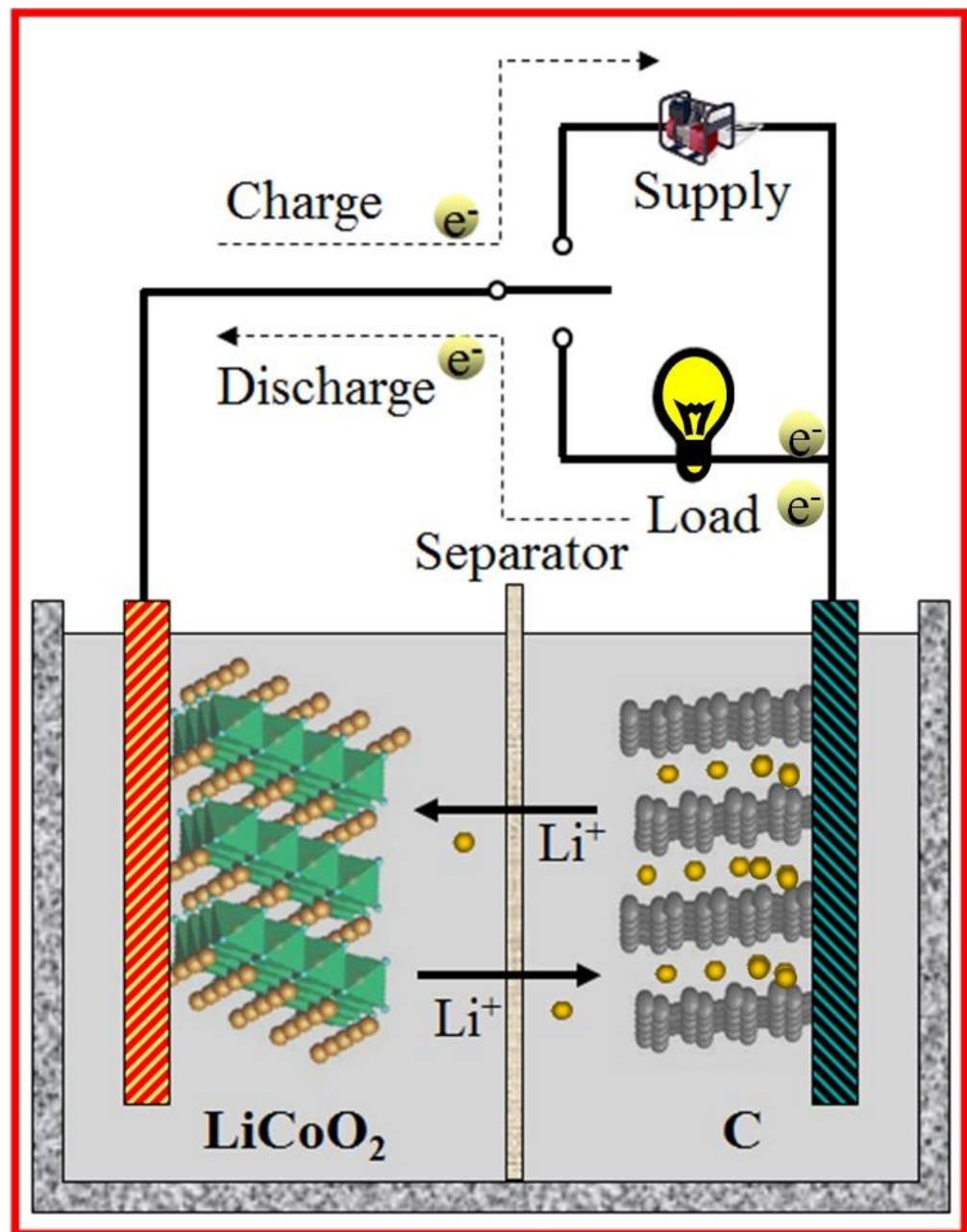


Figure 1. Diagram representing the operating principle of lithium-ion batteries. Reproduced with permission from [19].

The current commercialised anode material for Li-ion batteries is graphite, and, although it is cost-friendly, has high electrochemical stability, and is readily available, it has a specific capacity of 372 mAh/g [23,24]. Although graphite has a low specific capacity (372 mAh/g), it has replaced the hard and soft carbon that was initially used and played an instrumental role in the development of LIBs. This restricts the development of high-energy-density lithium-ion batteries and causes difficulties in recycling and rate performance [25,26].

The very limited capacity of graphite is evident when the battery is charging [27]. When the charging rate is higher than the rate at which lithium ions are embedded in graphite, the combined action charge overpotential and the ohm overpotential make the charge and discharge capacity very low [28,29]. This leads to a lithium metal coating on and around the graphite electrode. Normally, etching is used for graphite using a base such as potassium hydroxide (KOH) to create a channel similar to the edge surface, and the edge surface is increased so that the lithium ions choose the lowest energy path, and thus the diffusion length is significantly reduced. This is called a shortened diffusion path, which can pose some problems. The requirements may be too high, and the large pores will destroy the surface of the graphite [30,31]. The solid electrolyte interfacial (SEI) in a graphite-based lithium-ion battery should ideally be thin and have very little to no resistance, which is not easily attainable [32–34].

Silicon anodes have attracted a lot of attention due to their very high specific capacity of 4200 mAh/g [35]. Silicon is more expensive than graphite, and it retains several limitations that make it not easily applicable. Pure silicon is intrinsically a very poor conductor of electricity with additional limitations. These limitations include volume expansion during the lithiation process, which can lead to mechanical stress. The volume expansion of silicon causes the continuous breakdown and formation of the SEI, which in turn can lead to electrolyte consumption. Furthermore, the continued lithiation and delithiation of the silicon may lead to cracking of the internal material. This leads to extreme morphological changes and to a loss of contact between the current collector and the active material [36,37]. There have been several attempts to produce efficient silicon nanoparticles, but these proved to be slightly inefficient because of the high surface energy of the nanoparticles. During the insertion or extraction process and the resulting expansion or contraction, the particles begin to merge and, after some time, form large blocks which cannot take part in the reaction. The high cost of pure silicon and the challenges associated with its synthesis have limited its application in LIBs. Therefore, this prompted research attention to silicon carbides or silicon oxides [38,39]. One way to solve the problem is to coat silicon with carbon, which is an electronic and a conductor.

Silicon carbide (SiC) has a wide band gap that is characterised by a tenfold increase in the electric field and low intrinsic carrier transformation compared to silicon, and therefore it has emerged as a promising candidate for an anode material. Additionally, SiC has promising electrical, chemical, and electrochemical properties. The synthesis of SiC using conventional methods involves high energy consumption and very dangerous chemicals, which can be harmful to the environment [40,41]. To mitigate such issues, the use of a precursor sugarcane bagasse ash (SCBA) for the green synthesis of nanostructured silicon carbide is an environmentally friendly approach. Sugarcane bagasse is a by-product (waste) of the sugarcane industry which is abundant, inexpensive, and renewable, making it a good alternative to traditional material synthesis. Nanostructured SiC can be synthesised using the sol–gel method, combustion methods, or hydrothermal methods. The potential of waste-derived material, such as sugarcane bagasse, can be harnessed, and its synthesis is environmentally benign. This research not only aims to increase the performance of lithium-ion batteries but also complies with sustainable development goals and green chemistry [42,43].

Research in this field complies with Sustainable Development Goals (SDGs) no. 7, which focusses on providing clean and affordable energy, and SDG no. 13, which aims to reduce climate issues. Sugarcane bagasse is widely available and therefore serves as a suitable precursor for the synthesis of silicon carbides, providing a green alternative to traditional raw materials. The current literature aims to reduce synthesis costs by substituting expensive, less environmentally friendly, traditional raw materials with low-cost and renewable resources. A key objective of the investigation of sugarcane bagasse-derived SiC material is to show that it possesses enhanced or superior characteristics compared to those of commercial SiCs.

In summary, this approach to synthesising SiCs has been shown to be novel because it can repurpose agricultural waste and use it as a direct feedstock, adding value to low-cost and abundant waste material. The sustainable nature of the research could potentially influence a shift toward the use and continued study of sustainable energy storage systems.

2. Biomass

Biomass is a naturally occurring non-fossil fuel organic material that contains intrinsic chemical energy. It includes resources from agriculture, forests, and urban waste products [44], such as wood, sawdust, straw, manure, wastewater, and household waste [45,46]. Some of these are represented in Figure 2. Compared to fossil fuels, waste material releases fewer greenhouse gases, and the burning of fossil fuels leads to climate change and global warming, increasing the contents of so-called greenhouse gases (CO_2 , CH_4 , and NO_x) in the atmosphere. Biomass is plant material derived from a reaction between carbon dioxide (CO_2) and air, water, and sunlight via photosynthesis. It is efficient to process biomass either biologically or chemically by extracting the energy stored in the chemical bonds. The carbon is then oxidised to produce carbon dioxide and water. Since the process is cyclic, CO_2 is available to produce new biomass [47]. Some of the main reasons for the investigation of biomass are to somewhat mitigate the issues of climate change and global warming and to reduce the use of fossil fuels and our dependence on them. Biomass energy is one of the most abundant renewable energy sources, representing 10.4% of the total energy supply of the world and 77.4% of the renewable energy supply [46].



Figure 2. Some forms of biomass produced in nature [10].

Carbon has been known to be a very conductive material since the discovery of carbon black. The second most abundant element is carbon, right after oxygen. Carbon contributes to many food products and biomass production [10]. Of the huge amounts of biomass produced throughout the world, most of it comes from agriculture and forests and the residue that remains after harvests. Most of this biomass is burnt, but it can be used as a resource to prepare carbon-rich materials. Biomass can potentially also be used as feedstock. Sugarcane bagasse, which is produced in large amounts in South Africa, causes a large amount of pollution when it is not properly disposed of, which in turn attracts insects that degrade the surrounding environment. This problem can be solved by using the waste, burning it into ash, and using pyrolysis to convert it to carbon, which is cost-efficient, and the carbon produced has reasonable electrochemical properties for use in anodes [44,48].

Several carbon-filled materials have been experimented on over the years [49,50], for example, carbon nanotubes [51] and graphene, but, as expected, they do pose several problems, as they are costly. This can also affect their large-scale production [52]. Biochar, which is an organic material burnt in agriculture, has good structural and functional properties [53,54], making it very suitable as an anode material for LIBs and because it uses waste as a direct feedstock [55,56].

Biochar-based anodes are best suited for next-generation lithium-ion batteries because of their increased energy density. Graphite paper, for example, contains carbon derived from fossil fuel raw materials, and the use of such material generates a lot of pollution that is unfavourable to the environment. Plant biomass is made up of cellulose, hemicellulose, and lignin [57,58], which are polymeric compounds that decompose at temperatures between 200 and 600 °C in biochar preparation [59]. Electrochemical performance is enhanced because of the different electronegativities of the heteroatoms, which can also create more porous active sites, which in turn increases the reactivity of carbon materials. The use of biomass sources exhibits very good performance due to their stability, good conductivity, and promising cycle reversibility. This improves the performance of the anode material in LIBs [60].

As is commonly known, biomass is mainly due to our rapidly moving economy. Carbon-rich biochar derived from sugarcane waste can be used for many purposes, such as coating copper electrodes in lithium-ion batteries, which are listed in Table 2 [44]. The advantage of coating with carbon is that it ensures the stability of the SEI, thus preventing the inner SEI from being consumed. Carbon also has the potential to create stronger bonds between the surface material and the current collector. Biochar has amazing chemical and physical properties with great cyclability and exhibits increased overall performance. The abundant porosity, as well as the large surface area of biochar, can facilitate the diffusion of lithium ions and electrons [61,62].

Table 2. Applications and roles of biochar derived from biomass in lithium-ion batteries.

Roles of Biomass-Derived Carbon in LIBs?	Biochar Types	Properties of the Biomass	Max Specific Capacity (mAh/g)
Anode material	Hard/soft carbon, activated carbon	Conductivity, defect sites, porous, surface area	452 [63]
Dopant	Chitosan	Heteroatoms like N and O dopants	780 [64]
Binder	Chitin, chitosan	Polymeric nature, chemical stability	110.8 [65]
Separator	Cellulose	Insulator, flexibility, mechanical strength, chemical stability, wettability	1098 [66]
Current collector	Carbon cloth	Conducting, thin film, chemical stability, mechanical strength	212 [67]

Energy can be generated, transmitted, converted, and stored when necessary. Today, more than ever, it has become important to store energy, but this can be difficult. This may require expensive and bulky equipment. The main goal of many of the energy storage systems of today is not only to achieve high performance, but also to make them inexpensive and have longevity. These energy storage devices must also not harm the environment [68,69].

The type of energy that is stored is determined by a suitable energy device. Energy storage systems consist of a storage area and an energy conversion region [69,70]. The energy storage unit can be operated with the use of an inverter. For others, a rectifier converts the alternating current to a direct current [71,72]. This review will now focus on comparisons between silicon, graphite, and silicon carbides in LIBs.

3. Sugarcane Bagasse Ash: Pretreatment and Characteristics

Sugarcane bagasse ash is a fibrous material that remains after sugarcane stalks are crushed and the juice is extracted. It has a high chemical composition, as shown in Table 2. There are currently 14 sugarcane milling companies in South Africa. About 12 of them are in KwaZulu Natal Province and 2 of them are in Mpumalanga. The sugarcane industry in South Africa is an important exporter, exporting about 271 and 330 MTRV of sugarcane in the years 2011 and 2012. South Africa produces approximately 5% of the sugarcane produced worldwide and approximately 30% of the sugarcane produced in

Africa. The performance of silicon is usually improved by adding carbon to it. Carbon has a high conductivity; it has a very light mass coupled with a large surface area, which is what we need to essentially improve conductivity and mitigate the issues associated with silicon [73,74].

3.1. The Chemistry of Sugarcane Bagasse

Sugarcane bagasse cannot be used as feed for cattle and other animals, as the chemical composition within the cell walls limits it, making it suitable for commercialisation. Generally, sugarcane bagasse is composed of lignin, cellulose, and hemicellulose. The unequal composition is highly dependent on crop variety, climate conditions, growth location, and the physical and chemical composition of soil. The higher the amount of lignin in the bagasse, the less applicable it is on a large scale, as it becomes a major barrier to accessing carbohydrates. The low percentage of ash found in sugarcane bagasse (5%) serves as an advantage over other biomasses such as rice straw (17.5% ash) and wheat straw (11% ash) [75].

The chemical composition of sugarcane bagasse makes it an exceptional raw material for the synthesis of composite materials. The basic components of sugarcane bagasse are shown in Figure 3, with the elemental composition shown in Table 3 [73,76–78].

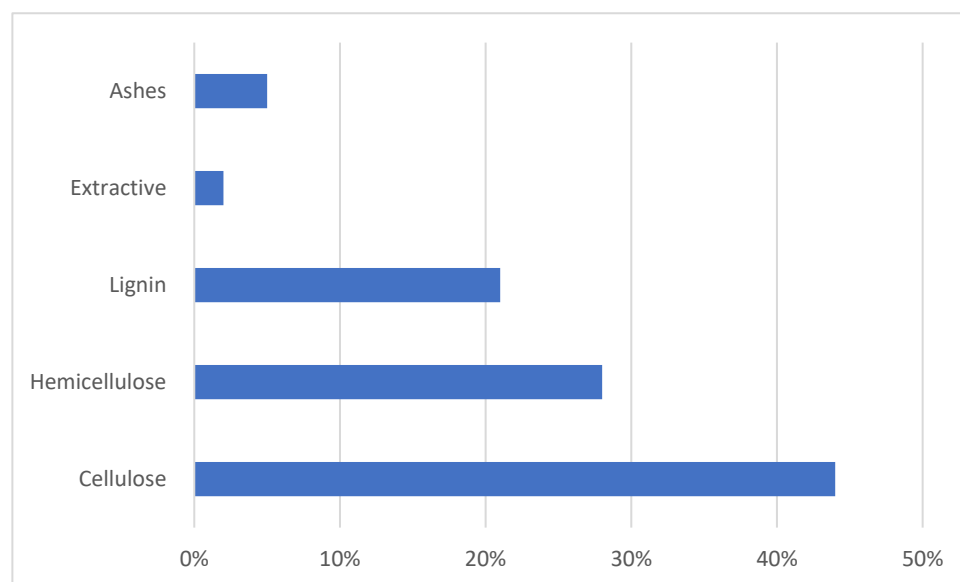


Figure 3. A graph showing different components found in sugarcane bagasse [79].

Table 3. The elemental composition of sugarcane bagasse in percentages (%).

Material	C	Si	O	Ca	Mg
Sugarcane bagasse	46.08–33.5	53.69–41.19	46.30–41.90	11.69–9.08	7.83–0.35

3.2. Pretreatment

Pretreatment is an important step in the conversion of lignocellulose to fermentable sugars. Using a thermochemical process, the aim is to separate the lignin and break down the lignocellulose structure. This process can be somewhat expensive with mature steps in the process of converting biomass particles. The preservation of pentose (hemicellulose) fractions limits the formation of degradation products. This minimises energy demand, and agents for pretreatment should ideally be cost-effective and be able to recycle the product inexpensively. Methods for pretreatment have been widely investigated, such as steam explosion, alkali washing, liquid hot water, and wet oxidation. Furthermore, the focus has been on acid leaching and thermal activation [80,81].

3.2.1. Chemical Activation

Chemical activation is a common method for the preparation of activated carbon. It is a process that involves mixing an activating agent with a raw material in a specific ratio to ensure complete impregnation. The most important aspect of this process is the penetration of the activating agent into a porous structure and its interaction with internal impurities, such as carbon, oxygen, and hydrogen. This results in an activated carbonaceous porous material with well-developed porosity. Some of the advantages of this type of activation are that it ensures minimum carbon burn, higher activation efficiency, higher activated carbon yield, and a lower activation temperature [82]. Chemical activation occurs at lower temperatures and for a shorter period compared to thermal activation. The development of a porous structure usually occurs during this step. Biochar is known to be an absorbent that generally absorbs certain functional groups from a medium. Activated biochar shows an increase in the absorption of lithium ions compared to that of biochar that has not been activated. This is due to the highly microporous surface and the abundant functional groups present in activated biochar. Chemical activation has many advantages over thermal activation due to its short activation time, low temperature, high surface area, and high reactivity [83,84].

Some of the chemicals that can be used for chemical activation include phosphoric acid (H_3PO_4), zinc chloride (ZnCl_2), potassium hydroxide (KOH), and sulfuric acid (H_2SO_4). Some of their effects on biochar have been summarised in Table 4 [85].

Table 4. Different chemicals and the effects they have on biochar.

Type of Activating Agent Used	Effect on Biochar
Phosphoric acid (H_3PO_4)	<ul style="list-style-type: none"> • Mesopore structure • Higher yield than fixed carbon content
Zinc chloride (ZnCl_2)	<ul style="list-style-type: none"> • Uniform distribution of micropores and mesopores
Potassium hydroxide (KOH)	<ul style="list-style-type: none"> • Defined and accessible pore structure
Sulfuric acid (H_2SO_4)	<ul style="list-style-type: none"> • Enlarges micropores and creates new mesopores. • Increases surface area and porosity

Chemical activation is usually conducted in two steps, where biomass is first carbonised to obtain biochar and then impregnated with an activating agent to obtain activated carbon [86]. The chemical agent can accelerate the decomposition process, while volatile solid matter is prevented from forming before activation [87]. Therefore, it produces activated carbon with a larger surface area. Therefore, chemically activated biochar also needs to be washed after it has been reacted by the acids to achieve a neutral pH. This is vital for battery functioning and to remove any impurities that may have formed during the activation process [88]. Chemical activation is crucial for experiments that require a unique pore structure [86], such as the experiments described in this review paper. However, this type of activation leads to equipment corrosion, chemical recovery, and potential secondary pollution [89].

3.2.2. Thermal Activation (Pyrolysis)

This process can be simply defined as the conversion of certain materials at high temperatures in an oxygen-free environment. Any temperature fluctuations and heating are known to have a direct impact on biochar. This process normally involves two steps: firstly, the carbonisation of sugarcane bagasse at elevated temperatures of 400 to 850 degrees Celsius, which is followed by the activation of biochar in the presence of an oxidising gas, such as carbon dioxide or nitrogen, at high temperatures of 600 to 900 degrees Celsius [90].

Biomass is made up of substances such as lignin, cellulose, and hemicellulose, and when it is pyrolysed the biomass will go through several temperature stages to eventually decompose into a carbon-rich material. The pyrolysis process helps to adopt the biomass into biochar; its texture is engineered using nitrogen gas. This is a safe and environmentally harmless process. This process helps develop hierarchical micropores in the biochar, which then modify the number of functional groups containing oxygen on its surface, which in turn leads to high-performance anodes. These procedures develop. Plant biomass is composed of lignin and cellulose; therefore, upon pyrolysis, the biomass goes through several temperature stages to allow for appropriate decomposition into carbon-rich material.

Pyrolysis can be classified into three types: fast, slow, and flash pyrolysis. The type of pyrolysis used in this review was slow pyrolysis, which is gradual heating in an anaerobic environment for a few hours to days at temperatures ranging between 300 and 650 degrees Celsius [91,92]. The low temperature coupled with a much longer residence time led to the production of good quality biochar. Volatilisation of carbon monoxide and carbon dioxide occurs at 100 degrees Celsius, and at around 200 degrees Celsius, hemicellulose, hexoses, and pentoses begin to decompose [87,93].

Typically, when temperatures are raised between 100 and 700 °C, acidic oxygen functional groups begin to decompose, for example, carboxyl, phenols, and lactones. The cellulose will then decompose at around 240 degrees Celsius [89,94]. The final component, lignin, breaks down at temperatures below 500 degrees Celsius. This eliminates all volatile components such as CH₄. This will result in a solid black powder—biochar—with a high crystallinity, surface area, and pore volume, as depicted in Figure 3. Temperatures should not exceed 500 degrees Celsius, otherwise silica may begin to form. Above temperatures of 600 degrees, oxygen begins to decompose [94,95].

4. Silicon Carbides

Silicon carbides have attracted much attention because of their remarkable performance and widespread application. Silicon carbide has several distinctive qualities, such as hardness, resistance to corrosion, and strength. Cellulose in sugarcane bagasse can easily be converted to carbon (C) and a significant amount of silica (SiO₂), specifically in the outer epidermis when reabsorbed by cell wall regeneration. The carbon and silica are in close contact with each other [89]. As a result of this contact and the large surface area, there are several small particles present. It is possible to synthesise silicon carbides (SiCs) at relatively low temperatures. These wastes are usually dumped or burnt, which can lead to the emission of very harmful toxins, such as methane and carbon dioxide [96]. Silicon carbides have a high critical breakdown voltage coupled with a high carrier drift saturation, making them suitable for application in third-generation conductors, such as energy storage systems. When silicon carbide was initially discovered, it was simply a product of a reaction between silicon and carbon. It has since gained attraction because of its quantum properties. Much of the power in modern energy storage systems is used to compensate for the safety margin in the power supply. This is not the same for silicon carbides, which can identify and compensate for local errors [89,97].

In Figure 4, silicon is covalently bonded with layers that alternate between silicon (Si) and carbon (C). In the tetrahedral structure in Figure 4, the carbon atom is connected to three silicon atoms inside the bilayer and has a single bond connected to a silicon atom. The length of the bond is 1.89 Å from the closest neighbouring Si atom to the carbon atom; 3.08 Å is the distance between two atoms of the same species in the SiC structure. Silicon carbide has numerous amounts of polytypes, but the most common ones are polytype 3H, which is cubic; hexagonal 4H; 6H polytypes; and rhombohedral 15R [89,98,99].

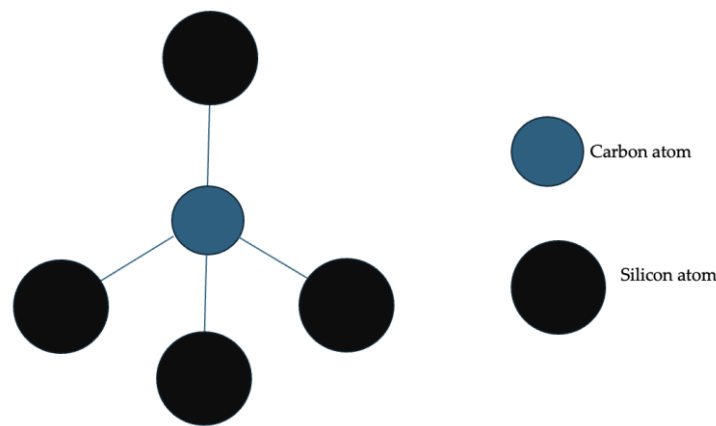


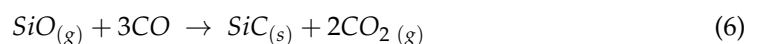
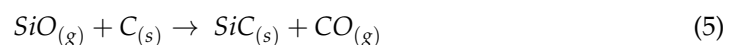
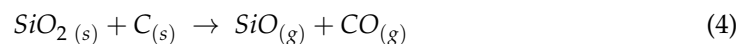
Figure 4. A silicon carbide molecule showing the tetrahedral bond between carbon and four silicon atoms.

4.1. Research Progress in the Synthesis of Silicon Carbides

Silicon carbides have exhibited remarkable advancements in recent years due to their unique properties. Modern day SiCs have low surface and are not conducive to wide range of materials. In order to enhance this, traditional synthesis methods have been adapted to increase not only the surface area but also the catalytic performance. Many strategies for synthesising traditional SiC are derived from carbothermal reduction it delivers high specific area [100]. The main focus being synthesising material that is porous and nanostructured.

4.2. Carbothermic Reduction

This technique is commonly used to synthesise silicon carbides. The synthetic method is carried out in an inert environment where carbon is mixed with silicon at high temperatures. The synthesis of silicon carbides from this method is conducted as follows.



Silicon carbide nanofibers and nanoparticles can be synthesised using carbothermic reduction. As catalyst carriers, SiC materials with a high specific surface area can be obtained through the preparation of SiC into nanoscale materials or through the direct preparation of nanoscale SiC materials. The nano-SiC synthesis process can be separated into two stages: nucleation and growth. First, SiO is mainly obtained by reaction (4), and it then reacts with solid carbon (5) to generate SiC nanoparticles (NPs) as “nuclei”. When the CO gas generated in the first two steps reaches saturation, SiO reacts with CO to form SiC nanofibers at the positions of the previously generated particles. Furthermore, reaction (7) also provides the CO gas required for reaction (6) to satisfy the requirement of a CO-saturated atmosphere. The carbothermic reaction consists of reactions/synthesis techniques such as the Acheson method, physical vapour deposition, carbon vapour deposition, and the sol-gel method when it comes to the synthesis of silicon carbides [100,101].

4.2.1. Acheson Process

The Acheson process is a typical carbothermal reduction process. The synthesis of silicon carbides was initiated by the Acheson process, which originated in 1892. They are synthesised in an Acheson electric furnace, which is still used to this day to produce polycrystalline silicon carbides. In this process, there is a solid-state reaction that occurs

between sand and petroleum coke at temperatures greater than 2500 degrees Celsius, forming silicon carbide as per the reaction in Equation (8).



The silicon carbide crystals are grown through the Acheson process in an electric-resistant Acheson graphite furnace, which is normally used for the synthesis of polycrystalline silicon carbides, making it suitable for grinding and cutting. This synthesis method normally leads to the formation of a large grain size that is contaminated with oxygen. Impurities such as aluminium and nitrogen can also be found that affect the electrical conductivity of silicon carbides [102].

Large strides have been made on an industrial scale using the aforementioned technique by synthesising fine-grained silicon carbides for use in construction ceramics. This consists of the synthesis of silicon carbide powder using the purified form of metallurgic silicon powder and soot. The quality of the study in question was tested, where silicon carbide was obtained by thermal activation of silicon and soot in an Acheson furnace at temperatures between 1300 and 1600 degrees Celsius. This led to the synthesis of pure silicon carbides (in the alpha and beta phases) with a granulometric composition that allowed the sintering of the catalyst to produce high-quality ceramics. This synthesised industrial material can resist chemical erosion and is able to maintain stability under high temperatures, as well as having low production costs and being environmentally friendly [103].

Further laboratory-scale synthesis of silicon carbides can be detailed using the Acheson method. An experiment was conducted in a partially open furnace; the power was increased by 2 V until the desired temperature of 1900 degrees was obtained. Where was the raw material that contained silicon? The core temperature was measured using a ratio pyrometer. Power was eventually reduced to maintain the core temperature [104].

4.2.2. Physical Vapor Deposition (PVD)

A very promising technique for the synthesis of silicon carbides is physical vapour transport (PVT), and this process is also known as seeded sublimation, which is a popular and successful method for growing very large single silicon carbide crystals. The first step is conducted in an ambient argon environment at 2500 degrees Celsius in a graphite container. Unfortunately, the method leads to uncontrollable nucleation and dendrite-like growth. This is due to the uncontrollable growth of silicon carbides. The PVD technique involves layering Si and C layers several times using direct current magnetron sputtering or through distinct approaches where silicon is most likely deposited using the above-mentioned method. Carbon is then used as the first layer to allow better adhesion [99].

PVD techniques, such as sputtering, and evaporation have better control over the uniformity of the film and the thickness. Therefore, this results in the formation of thin films and uniform layers of silicon in current collectors. This technique can be used for large-scale production in a way that ensures the same quantity as in laboratory-scale production. It also allows for the synthesis of electrode material that has very good adhesion and resistance to degradation. The fabrication of the electrode involves the use of additives and binders to hold the active material together but also to improve electrical conductivity. This can also prevent the electrode from performing optimally by reducing the reaction time and increasing the resistance to ion transport. The PVD method allows for direct interaction between the current collector and the active material by eliminating binders and active material, reducing the cost of manufacturing and increasing overall conductivity [105].

4.2.3. Carbon Vapour Deposition

Another traditional method for synthesising silicon carbides is carbon vapour deposition. This is a process that allows gaseous species that are in proximity to the substrate or the surface to be directly absorbed onto that surface. This leads to solid-state growth of the catalyst. This technique allows for the growth of different shapes of silicon carbides, pow-

ders, and whiskers. This process can be time-consuming and requires special conditions, such as argon flowing through the reaction.

Major advances could be seen as early as 2010 when Qiaomu Liu synthesised zirconium carbide and silicon carbide hybrid whiskers using CVD. The experiment was carried out at a temperature of 1250 degrees Celsius, which unfortunately caused the formation of carbon and silicon drops, with the size of the droplets determining the diameter of the whiskers [106].

Wang, H et al. further improved this method by using CVD for the homoepitaxial growth of silicon carbides. Hydrogen or argon are usually used as precursors, and the growth temperature is usually between 1500 and 1650 degrees Celsius. The growth of epitaxial SiC normally creates silicon droplets that render a battery useless. Efforts have been made to increase the temperature to allow these so-called particles to evaporate. The use of hydrochloric acid for epitaxial growth is one of the simplest processes and involves simply adding HCl to the solution. This process uses low temperatures of 1300 degrees Celsius [107].

In a more recent paper, the growth of in situ stable silicon carbide-reinforced silicon nanosheets from organoclay and certain amounts of Ca-Mnt was investigated. The organoclay was added to a cv solution, stirred, centrifuged, and dried until the CV-Mnt precursor was obtained. The product was then carbonised at 600 degrees Celsius for 3 h in an inert environment. After further acid treatment and vacuum drying, silicon carbide was obtained. To test the electrochemical performance, a coin cell was prepared in which it could cycle between 0.01 and 1.5 V, with a discharge capacity of 3300/2633 mAh/g [108].

4.2.4. Sol–Gel Method

Si carbide precursors are normally synthesised by mixing silicon with a carbon source; the sol–gel method can, however, be used to ensure uniform mixing of silicon and carbon sources. Na described a route to prepare silicon nanoparticles using the sol–gel method. This sol–gel method was developed to produce a phenolic resin–TEOS hybrid gel, using hydrochloric acid (HCl) as a catalyst to produce SiC by carbothermal reduction of the specific gel. Silicon carbide nanoparticles were obtained by reducing the gas between temperatures of 1400 and 1500 degrees Celsius. The particle size distribution increases with an increase in temperature, therefore increasing temperature [109].

Since then, the method has been tried and improved; Li et al. used the same sol–gel method to develop silicon carbide whiskers. It is a convenient and low-cost method, with the potential to be developed at an industrial scale, to fabricate nanostructured SiC whiskers, including a sol–gel process involving water-soluble phenolic resin and silica sol and carbothermal reduction between the phenolic resin and silica. The products were nanosized SiC whiskers. These silicon carbide whiskers exhibited very high crystallinity with the intracellular space being 2.5 Å, which is very close to the theoretical lattice spacing value of 2.174 Å [110].

Another study reported the successful synthesis of silicon carbide powders using the solvothermal assisted sol–gel process. Here, analytical grade tetraethyl orthosilicate (TEOS) and ethanol were placed in an oil bath with an appropriate amount of phenolic resin. Carbothermal reduction was performed at temperatures between 1400 and 1600 degrees Celsius for one hour. This type of synthesis showed outstanding advantages over the powders produced by hydrothermal/solvothermal processes, including excellent homogeneity and a narrow particle size distribution. The synthesised silicon carbides displayed more agglomeration of the particles, therefore showing that the particles had an increased surface area and maintained their homogeneity after pyrolysis. The synthesised SiC indicated a value of 2.17 Å, which is very close to the theoretical value of 2.174 Å [111].

The modified method mentioned above was used to synthesise SiC-B₄C, as reported elsewhere [112]. The experiment used tetraethyl orthosilicate (TEOS) as a source of silicon. Silicon, carbon, and boron were also used, using the methodology tabulated in the figure below. Normally, TEOS is exposed to methoxide alone, but here it was exposed to boron

before the methoxide. The main objective of this specific paper was to improve or modify the use of binary sol, as the different hydrolysis rates lead to the segregation of the synthesised sol, making it unsuitable for the synthesis of carbides. To mitigate this problem, an alkoxide (boron methoxide), which has a low hydrolysis rate, was used. Boron hydroxide is hydrolysed much faster than TEOS [112]. The Si-B4C was synthesised at a temperature of 1350 degrees Celsius. The surface of the material was porous and had a surface area of 172.92 m²/g. pH was also an important factor in determining the stability of the particles within the sol. The pH increased from 4 to 7, therefore lowering the stability of the solution and increasing the particle size [94].

4.3. Advancements in Green Synthesis of Silicon Carbides

Recently, there has been an increased focus on more cost-effective ways of synthesising silicon carbides [113–116]. Silicon carbide is not abundant in nature and is almost completely absent, and it is usually found as stardust around carbon-rich stars. As a result of its scarcity in nature, efforts have been devoted to its synthesis. Naturally, a green approach for the synthesis of silicon carbides would be ideal, and the search for one has, of course, gained a lot of attention, primarily to mitigate the cost issues that may arise [115,116].

Hossain, Sakib Tanvir, Fatima Tuz Johra, and Woo-Gwang Jung synthesised high-purity silicon carbides using recycled silicon wafer particles. The silicon wafer sludge contained a small number of impurities, silicon, ethylene glycol, and cooling water. In the process, SiC was synthesised using the carbothermal process. The silicon sludge was mixed with carbon at different molar ratios. The mixture was then turned into pellets and placed in alumina crucibles and treated with heat at temperatures between 1400 and 1600 degrees Celsius. A much higher amount of SiC was formed at 1550 °C from a mixture with a Si sludge-to-C molar ratio of 1:1.4 than from mixtures with 1:1.2 and 1:4 molar ratios at 1400 °C and 1600 °C, respectively. To remove excess carbon, we heat-treated the product at different temperatures. We assume that excess carbon leaves the reaction as CO₂ or CO when heated (750 degrees Celsius) in the presence of air, resulting in a general better morphology [117].

Sun, Kaidi, and others performed a clean and low-cost synthesis of beta-silicon carbides with the residue from carbon fibre and sandstone. The purity of these beta silicon carbides produced using these inexpensive materials in an argon atmosphere at 1600 degrees Celsius was 98% [116].

Zeraati, Malihe, Kazem Tahmasebi, and Ahmad Irannejad found a way to synthesise silicon carbides at a temperature of 800 degrees Celsius over 3 h using molasses, sugar, and stevia externa, which are plant extracts. Green synthesis was applied using the sol-gel method. The use of low temperatures ensures that only the impurities are removed and not the carbon present [118].

5. Synthesis of Silicon Carbide Using Sugarcane Bagasse

The synthesis of silicon carbides extracted from sugarcane bagasse ash must be conducted in steps: first, silica is synthesised from the ash, followed by reduction to silicon, and then silicon carbide can be synthesised from silicon.

In the silica synthesis, 1M hydrochloric solution and 2.5 M of HCl were used for the pretreatment of the ash and precipitation of impurities. Then, 1 M sodium hydroxide was prepared to extract a sodium silicate solution from the sugarcane ash. The ash was treated with acid to remove any oxide compounds, after which 100 g of ash was suspended in 600 mL of hydrochloric acid and then stirred with a magnetic stirrer at room temperature for 2 h. The ash was filtered and washed until a neutral pH was achieved. The ash was then dried in the oven for 5 h. The dried acid-treated ash was then immersed in 1M sodium hydroxide with ash-to-base ratios of 1:5, 1:8, and 1:10 *w/v*. The mixture was then heated for one hour at a temperature of 90 °C. The mixture was then cooled to room temperature. The residue was then filtered off, and the filter cake was washed with hot water. The filtrate, sodium silicate, was mixed with a base to obtain a neutral pH. Then, it was left at room

temperature for 24 h to undergo an ageing process. The silica that formed was washed with hot water and dried at 100 °C for 5 h [87,119].

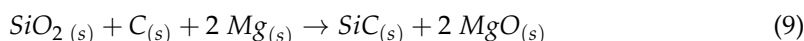
A gas detector in an exhaust line was used to reduce a mixture of 1 mol of silica and 3 mol of carbon powder in a crucible containing 100 mg of powder. The next steps involved the synthesis of silicon carbide; so, after thermal treatment, a 4% solution of 4 grammes of NaOH in 100 mL of distilled water was extracted, and sodium silicate was produced as a product. For the sol–gel process, the solution could be titrated with an acid such as HCl (hydrochloric acid) to form silica [120].

Sugarcane bagasse consists of silica and carbon, allowing it to be synthesised into silicon carbide. As shown in Figure 5, SiC was produced using magnesiothermic reduction at a temperature of 600 degrees for 6 h. There are several steps in this synthesis process, and the first step is carbonatisation of the silicon bagasse. Acid treatment then leads to the formation of SiC. The authors used a technique like that used above, where hydrochloric acid was used to remove any impurities, with magnesium oxide resulting from a magnesiothermic reaction. Magnesium powder was used as a catalyst to synthesise silicon carbide. Nitric acid (HNO₃) was used to remove any residual silica. The dried sugarcane bagasse was placed in a 600-degree Celsius furnace for one hour in an argon-rich environment [88,121].



Figure 5. Synthesis pathway of silicon carbide (SiC) extracted from sugarcane bagasse.

The magnesium powder could then be mixed with sugarcane bagasse in a 1:2:5 ratio (mass/volume). The mixed sample was heated at 600 degrees Celsius for 6 h. The MgO was dissolved in 1 M hypocaloric acid under constant stirring at room temperature. Using distilled water, the sample was washed, then heated for an hour at 700 degrees Celsius to remove any residual carbon. In 50 v/v% of HNO₃, the sample was immersed to dissolve SiO₂. The sample was then washed and dried, resulting in silicon carbide [122]. The synthesis pathway is represented in Figure 5 and the overall reaction is represented in Equation (9) [79].



Agricultural waste is a good candidate for the synthesis of SiC because it absorbs Si from the earth's crust after oxygen has been released into the soil by biological and chemical processes. The take-up of silicon from the water in the soil is in the form of silicic acid H₄SiO₄, which is then polymerised as amorphous silica (SiO₂) [123].

Silicon carbide was synthesised from sugarcane bagasse using a pyrolysis process using agricultural waste, such as sugarcane extracts, peanut shells, corn cobs, and rice husks, all of which were combined to form a powder mixture by ball milling. This mixture was then kept in a microwave at temperatures of 160, 170, and 180 degrees Celsius for different times—160, 170, and 180 min, respectively. After SiC was obtained in the form of a powder, it was kept in a vacuum [124].

5.1. Characterisation of Silicon Carbides Synthesised from Sugarcane Bagasse: Techniques That Can Possibly Be Used for Analysis

Characterisation techniques, especially those for morphology and surface properties, are essential in material science. They provide an understanding of a material and how to manipulate its surface properties.

Figure 6a,b, which are SEM images of the SiC synthesised from sugarcane bagasse, depict a crystalline nature and irregular shape like those of other anode materials in lithium-ion batteries such as graphite [122]. The SEM image shows that the cycled electrodes maintained their structure and performance; this implies that there were almost no volume changes or expansions, which cannot be said for Si anodes. Therefore, a lot of space is needed to compensate for volume changes in silicon anodes [125]. The results from the above EDX analysis in 6c clearly suggest the presence of silicon and carbon as predominant elements in the spectra. The presence of silica (SiO_2) can also be observed due to the presence of oxygen, suggesting the successful synthesis of SiC.

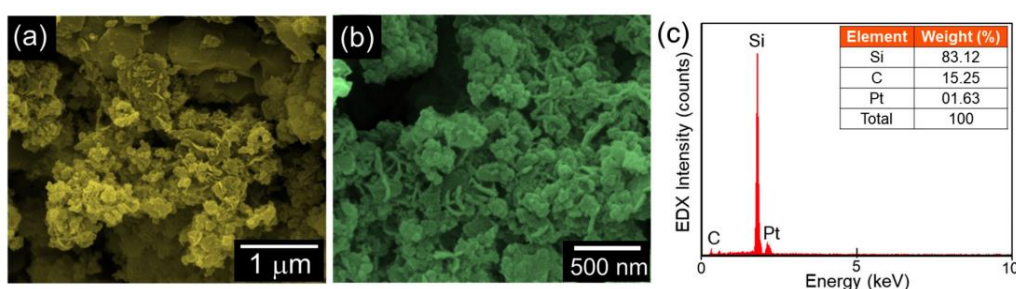


Figure 6. (a,b) SEM images of silicon carbides synthesised from sugarcane waste and (c) SEM-EDX spectrum for SiC, adapted with permission from [125].

5.1.1. Fourier-Transform Infrared Spectroscopy

The FTIR spectra of SiC synthesised using sugarcane bagasse as a raw material are shown in Figure 7. The characteristic bands can be observed at 1106.28 cm^{-1} (Figure 7a) and 1096.37 cm^{-1} (Figure 7b). These are strong absorption bands, which indicate the binding of carbide to the surface of silicon. The binding mechanism is mostly facilitated by the sp^2 -hybridised carbon content, which is further confirmed by characteristic absorption bands seen in the 1600 to 1700 cm^{-1} regions [122].

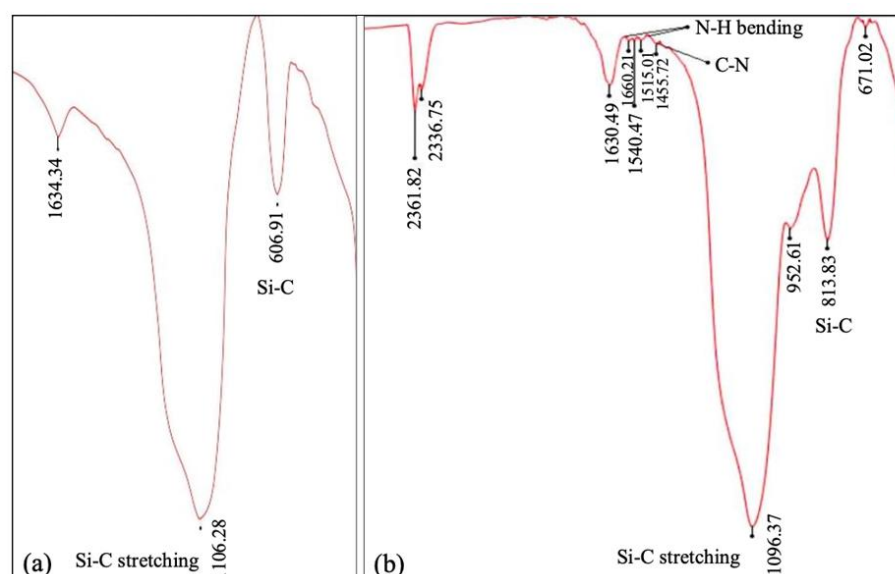


Figure 7. (a,b) FTIR spectra of SiC synthesised from sugarcane bagasse. Reproduced with permission from [122].

5.1.2. XRD and Raman Spectroscopy

Figure 8a shows the XRD pattern of the C-Si nanocomposites. Diffraction species can be seen for Si and carbon. There are six clear diffraction patterns, namely, at 28.2° , 47.1° , 56.1° , 69° , and 87.9° , which correspond to (111), (220), (311), (400), (331), and (422) lattice crystal planes for the crystalline silicon, phases (002) and (100) being activated carbon. The sample shows intrinsic vibration from only Si and C for the Raman spectroscopy measurement. Displayed in Figure 8b are predominant Raman bands at 514 , 959 , 1341 , and 1590 cm^{-1} from carbon and silicon. The vibrations at 1341 and 1590 cm^{-1} arose from D (sp^3 type) and G (sp^2 type), which are bands of graphitised carbon [125].

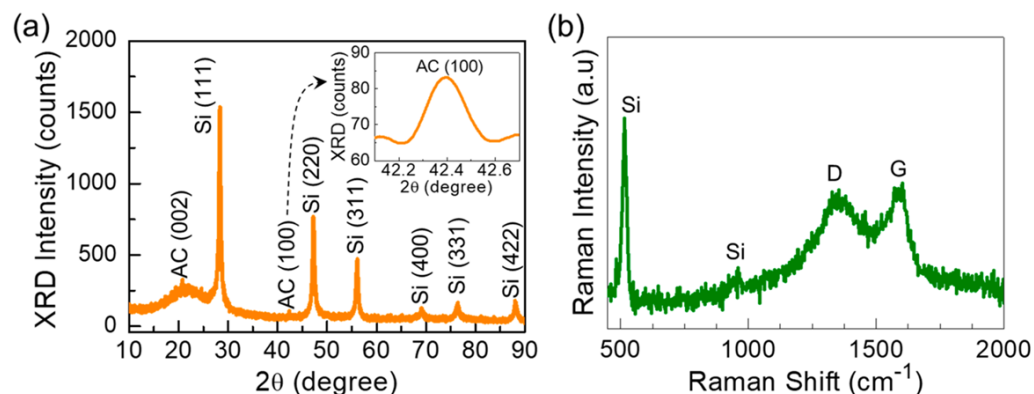


Figure 8. (a) XRD for silicon carbides synthesised using a D2 phaser system. (b) Raman spectrum of sugarcane bagasse synthesised using a LabRAM HR800 (HORIBA Jobin Yvon Inc., Edison, NJ, USA) [125].

5.2. Performance of Silicon Carbide in Lithium-Ion Batteries

The SiC nanocomposite was evaluated for its electrochemical properties. The discharge capacity in Figure 9a is due to the insertion of guest Li^+ ions into the silicon lattice host to transform the crystalline silicon into Li_2Si in the amorphous phase at 0.3 to 0.5 volts. The specific charge and discharge capacity, which are for silicon macroparticles, are shown at 1250 and 620 mAh/g, the irreversibility being 51.4%. The silicon nanoparticles show a specific charge, with a discharge capacity of 700 and 420 mAh/g and an irreversible percentage of 40%. The higher the irreversibility percentage, the deeper the diffusion of Li^+ ions into the bulk silicon and the formation of an aggressive SEI, whereas silicon carbides provide charge and discharge capacities of 1125 and 350 mAh/g, with an irreversibility percentage of 70%, as depicted in Figure 9a. There is more irreversibility in silicon carbides as anodes than in silicon macroparticles and nanoparticles; thus, they form a stable SEI [126].

In Figure 9b, silicon carbides have a discharge capacity of 300 mAh/g with 85.7% retention compared to a fresh cell with 92.3% retention after cycling. The silicon nanoparticles have an irreversibility of 200 mAh/g with 47.6% retention compared to a fresh cell, with an increased retention of 98.5% after 10 cycles. In terms of retention, this refers to more surface lithiation compared to deep lithiation after ageing for 10 months. Silicon microparticles have an irreversibility of 50 mAh/g with 9.6% retention compared to fresh cells with 96% retention [124,126].

An author reported the mechanical properties of silicon carbides considered electrochemically inert to Li^+ . This property strengthened the composite electrodes, allowing them to control the charge and discharge rates and therefore influence the volume changes [126].

6. Challenges and Prospects

Currently, there is a large demand for silicon carbides, especially as a sustainable production route and application in the energy industry. Although biomass has several advantages, it is an excellent carbon source while additionally acting as a good template for the synthesis of various carbon-based materials, making it a good candidate to overcome the

energy crisis. However, the use of the mentioned bagasse suffers from several challenges, such as irregular morphology and limited surface area [127]. Therefore, it is important to find a suitable heteroatom for doping. Achieving optimal material purity for silicon carbide can be challenging, as sugarcane bagasse ash may have impurities, such as silica, which affects the electrochemical performance of the anode material. The synthesis process of nanostructured silicon carbides from bagasse on a large scale can be difficult, especially when trying to maintain the consistency and quality of the material. Extensive optimisation is required to achieve nanostructured SiC with a good surface morphology, crystallinity, and particle size. It is also important to ensure that the electrochemical integrity of the SiC is not compromised, so that the battery may have sufficient useful life. Future research can also focus on how to improve some of the above-mentioned limitations, such as retaining as much yield as possible. Doping silicon carbides with urea increases their functionality, so a broad focus should be placed on this [128,129].

Several other challenges need to be addressed to possibly improve the performance of these silicon carbides. Specifically, the purity of the synthesised product and the purity of the product can present certain issues, especially when it comes to certain applications. For instance, in the application of composites, the issue of purity is not relevant, but for applications in the electronic field, the purity needs to be high. Biomass is made up of not only carbon but also a lot of inorganic material. Trace materials tend to be found in silicon carbides. However, certain techniques such as chemical and thermal activation can be used to reduce the impurities present. It is not certain that the impurities are completely removed, as the above-mentioned activation methods have limitations. Thus, there are still improvements that could be made to the study. There have been several studies on the synthesis of SiC extracted from biomass, all of which show that there is no control over the surface morphology [130,131].

Future research can also focus on the relationship, structure, and performance of cubic, rhombohedral, and hexahedral SiCs. A wide selection of silicon carbides can be used for applications. Extensive research on the performance of SiC at extreme temperatures can be conducted. In-depth research has been carried out on β -SiC but not so much on α silicon carbides [132–134]. Researchers can focus on synthesising SiC at low temperatures below 1000 degrees Celsius. The achievement of sugarcane bagasse-derived carbon material with high performance and cost-friendliness is a future-demanded goal.

7. Conclusions

Due to the growing energy demand, the use of energy storage systems, such as lithium-ion batteries, has attracted a lot of interest. Currently, many scientists are looking to develop cost-friendly, high-performance, and durable materials. Biomass is a suitable candidate for the synthesis of carbon-rich materials because of the presence of heteroatoms such as carbon, hydrogen, and nitrogen. It can be used as an electrode material in lithium-ion batteries. This review paper examined lithium-ion batteries in detail and what makes them stand out in comparison to other energy storage devices. Different biomass precursors and what made sugarcane bagasse the most suitable for this research were discussed. Different activation methods, such as chemical activation and pyrolysis (thermal activation), and the effects they had on the material were considered, as were the different components and characteristics of sugarcane bagasse and how sugarcane bagasse can be used to synthesise silicon carbides. In fact, two-dimensional structures, such as nanotubes, nanowires, and silicon nanoparticles, enhance the performance of lithium-ion batteries. Their primary disadvantages are that they are costly and have a complicated production process with a low tap density, which reduces the application of silicon as an anode material in lithium-ion batteries. In contrast to nanostructured silicon material, which has very low production costs and high tap density, nanostructured silicon material has increased stability when it comes to the production of silicon anode materials. A good knowledge foundation has been created for the synthesis of silicon carbides. SiC presents good morphological and structural properties, as can be seen from the SEM images shown in Figure 6a,b. The SiCs

also have strong stretching peaks showing their sp^2 -hybridised structure. With the presence of Si-O stretching in Figure 9a, SiC has 85.7% retention compared to a fresh cell with 92.3% retention after cycling.

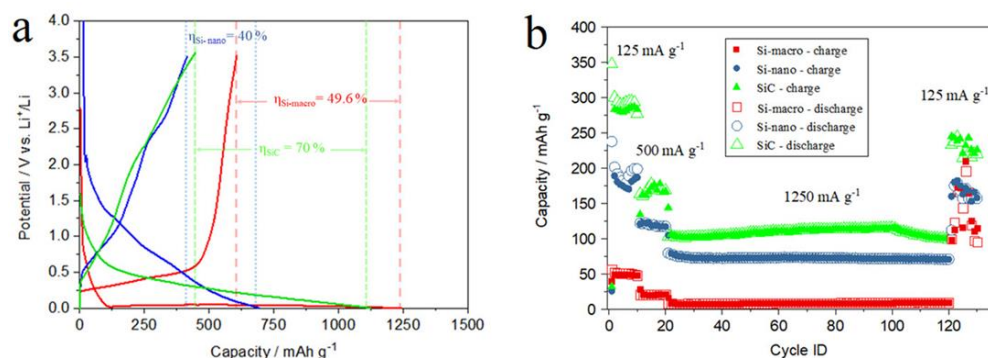


Figure 9. (a) The capacity in terms of charge and discharge of silicon carbides, silicon macroparticles, and nanoparticles and the percentage irreversibility of each. (b) Comparison of silicon nanoparticles, silicon microparticles, and silicon carbides after 10 months of ageing. Reproduced with permission from [126], © 2020 Elsevier B.V.

For any future studies, silicon carbides show increased performance in comparison to their silicon counterparts (silicon nanowires, silicon nanotubes, and silicon nanoparticles). Biomass-based silicon can be successfully synthesised and applied for use in energy storage systems such as lithium-ion batteries. Different approaches have been used to produce silicon carbides, but the main overlap in most of the literature is the incorporation of treatments, be they thermal or chemical. The methods mentioned above can be used to synthesise SiC, and they also make available an environmentally friendly way to reduce waste.

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