



## Review article

# Advances in silicon–carbon composites anodes derived from agro wastes for applications in lithium-ion battery: A review

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## ABSTRACT

Recently, the growing demand for high-performing batteries and different environmental challenges (such include global warming and climate change) have increased the requirement and demand for Lithium-ion batteries (LIBs) used in advanced technologies (i.e., electric cars and many others). To meet this increasing demand, there is an urgent need for more advanced technologies and materials. In the pursuit of developing anode materials, silicon has emerged as the utmost favourable choice for the next generation of LIBs, aiming to substitute the commonly used graphite. Carbon is commonly used to render silicon (Si) suitable for use since Si cannot be used directly as the electrode in LIBs. One of the recently discovered techniques in the development of high-performance LIBs is the use of inexpensive, sustainable, renewable, and eco-friendly materials. Agro-waste-derived silicon and carbon are often used as long as they don't negatively affect the LIB anode's performance. This review paper presents the advances in the development of silicon-carbon (Si/C) composite anodes sourced from agro-waste for applications in LIBs. It provides an overview of agro-waste-derived silicon-based anode materials and techniques for extracting silica from agricultural wastes. Next, the outline explains the preparation technique of Si/C composites obtained from agricultural residues for use in LIBs. Additionally, the paper delves into recent research challenges and the potential prospects of materials derived from agro-waste in the advancement of sophisticated LIBs battery materials.

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## 1. Introduction

Increasing industrial activities, dependence on fossil fuels and population growth cause related environmental issues (i.e., pollution) and increase in energy demand [1]. To lessen reliance on fossil fuels and ease the strain on energy demand, the mainstream strategy concentrates on the development of sustainable energy technologies, particularly electrochemical energy storage systems with the benefits of flexibility, high efficiency, and safety. Though, of all the electrochemical energy storage, LIBs demonstrate the most potential and capability for performance [2]. The significant growth of LIBs in contemporary society can be attributed to the widespread use of electric vehicles (EVs), military equipment (i.e., drones, gear and uniforms) and mobile electronics (i.e., notebook computers, mobile phones etc.). However, the high cost and scarcity of anode materials (e.g., lithium and other raw materials like cobalt and nickel) for LIBs production remain the drawback despite the increase in demand [3]. These problems lead to an endless search for more affordable, environmentally friendly battery solutions. Recently, Biomass (i.e., agro waste) derived carbon materials have attracted significant attention as potential materials for anode used in LIBs due to their advantageous characteristics, which include their sustainable manufacturing, simple accessibility, environmental friendliness and affordability. So far, carbonaceous materials from different biomass sources have been studied extensively for use as LIB anodes [4]. Important features of Biomass-derived carbon are high specific surface area and porous architectures needed to improve diffusion and ion transfer.

### 1.1. Different anodes materials used for applications in lithium-ion battery

The most common anodes on the market right now are made of alloys, metal oxides, and graphite, among others. Graphite is commonly utilized as the anode material in viable LIBs due to some interesting properties such as excellent cycling stability and good electrical conductivity but low theoretical specific capacity ( $372 \text{ mAhg}^{-1}$ ) limits its usage for LIBs applications. Also, graphite is either artificially produced or mined which makes it expensive [5]. Silicon is the most chosen material for next-generation LIBs due to its natural availability, low working potential, nontoxicity and high theoretical specific capacity ( $3579 \text{ mAhg}^{-1}$ ). Also, silicon anode has lower de-lithiation potential when compared to other anode materials. To produce silica, silicon nitride, silicon, graphene and silicon carbide, rice husks are the most remarkable carbonaceous and siliceous precursors [6]. However, silicon-based anodes have a lot of drawbacks. For example, the massive volume expansion ( $\sim 300\%$ ) that occurs during lithiation/de-lithiation can cause fractures, mechanical stress and the silicon particles pulverisation after several cycles, which significantly weakens the anode's ability to transport lithium ions. This often leads to the reconstruction of the "solid electrolyte interphase (SEI) layer", electrode polarization [7], continuous capacity decay and poor coulombic efficiency. Additionally, using silicon as the LIB anode may result in the production of an inactive phase of lithium silicate during the early irreversible charging and discharging period. This might affect the whole electrical conductivity of the anode and considerably reduce the initial coulombic efficiency of the LIB [8]. In addition, the production of silicon-based anodes is costly, and complicated which limits its application in the industry [9,10].

Much research work has been done to overcome the drawbacks of using silicon anodes including silicon/carbon composting [11] and converting silicon to nanopillars, nanotubes and nanowires to relieve the physical strain in the anode. However, the methods used in the synthesis of the nano-silicon anodes are sensitive and energy-intensive, which limits their scalability and practical applicability [12]. Silicon/carbon composite is being considered extensively because of its excellent operability while carbon offers high electrical conductivity and cycle stability. Hence, the anode with a high specific capacity will have improved electrical conductivity if carbon is added to silicon [13,14]. Furthermore, the outer shell of carbon can operate as a buffer between the silicon and electrolyte, preventing direct contact, generating a stable solid electrolyte interphase coating and lessening volume variation during charging and discharging. Also, the addition of carbon to the silicon helps preserve the electrode's structural integrity. Therefore, carbon and silicon counteract each other's mechanical instability, low specific capacity, and poor electrical contact, the combination appears promising. Also, the Si/C anodes exhibit outstanding cycle stability and lithiation [11].

The production of Si/C anodes started with Wilson et al. [15] when the authors embedded 11 % of "atomic silicon in pre-graphitic carbon". Ever since, numerous studies have been conducted, which has improved the Si/C anodes' performance. For instance, Cui et al. [16] produced "nanowires with a Si/C core-shell structure". Despite the advances, there are still some challenges including expensive raw materials, complex synthesis processes and some raw materials that are not environmentally friendly [17]. Meanwhile, an essential strategy in achieving environmentally friendly and low-cost raw materials is the extraction of Si/C anode from eco-friendly, naturally occurring and recyclable materials (i.e., Agricultural waste). Agro-wastes contain a huge percentage of inorganic constituents and various Si/C anode materials for Lithium-ion batteries have been produced from different resources.

The review paper focuses on the advancement in the development of silicon-carbon composite anodes produced from agro waste for LIBs applications. The synthesis techniques used in the production of silicon-based anodes from agro-waste were discussed. Then, the processes in the development of Si/C composite anodes derived from agro-wastes for lithium-ion batteries were described.

## 2. Agro-waste derived silicon-based anodes materials

Agro-wastes have huge deposits of phytoliths as Amorphous Silica ( $\text{SiO}_2$ ), utilized as a precursor to the synthesis of Si. The production of silicon from agricultural waste for LIBs application is simple and inexpensive. Silicon from agro-wastes is extracted through either calcination or acid purification process [12]. Silicon is the most abundant element but its concentration in agro-wastes is low when compared with primary minerals. Nevertheless, agro-waste can be a potential source for silicon extraction due to the vast quantities of agro-waste produced globally. The development of contemporary LIBs may profit from the accessible Si produced from

biomass.

## 2.1. Extraction of silica from agricultural wastes

Extraction of silicon from agro-wastes involves different processes which include thermal treatment and leaching process. Agro-waste consists of organic matter and some impurities. For instance, silicon is the main constituent of plant agro-waste (i.e., rice husk) with some other metal oxides like  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Sr}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{CuO}$ ,  $\text{TiO}_2$  and others [18]. The leaching process is an effective technique to remove impurities from agricultural waste using concentrated acids. According to Muraleedharan Pillai et al. [12] the leaching process begins with the removal of contaminants using an acid such as hydrochloric acid or sulfuric acid. Hydrochloric acid is the acid that is most frequently employed in this procedure. Before the leaching process, the agro-waste is first crushed using the ball milling technique, the particles obtained from the milling process are then mixed with 10 % of hydrochloric acid at 70–120 °C for a period of 2–12 h to remove all metallic impurities. The final stage is washing with deionized water and then filtering to obtain the purified Si which is later dried for 5–12 h at 60–120 °C [19,20]. Also, alkali fusion can be used to remove impurities, this is done by fusing the obtained particles from the milling process with an alkali (i.e., sodium carbonate;  $\text{Na}_2\text{CO}_3$ ) at high temperature [21]. This process converts silica into a solution made of water and soluble sodium silicate. The resulting solution can then be treated to precipitate silica by adjusting the pH or by adding a mineral acid.

For some agro-waste, the leaching process result in silica ( $\text{SiO}_2$ ) production and it require further processing which is conducted through thermal treatment. The thermal treatment process is usually performed at a temperature within the range of 550 and 800 °C at a heating rate of 2–5 °C/min for 2–6 h in air [22]. During the process, the agro waste organic components (i.e., hemicellulose, lignin and cellulose) burn out, leaving behind the silicon. The crystal structure of the silica either crystalline or amorphous largely depends on the calcination temperature. Different kind of silica is produced in the thermal process such as nanoporous silica with pore diameter and surface area within the range of 3–8 nm and 101–329  $\text{m}^2\text{g}^{-1}$  respectively [20] and silica spherical nanoparticles with about 40–90 nm [6].

## 2.2. Reduction of silica ( $\text{SiO}_2$ ) to silicon (Si)

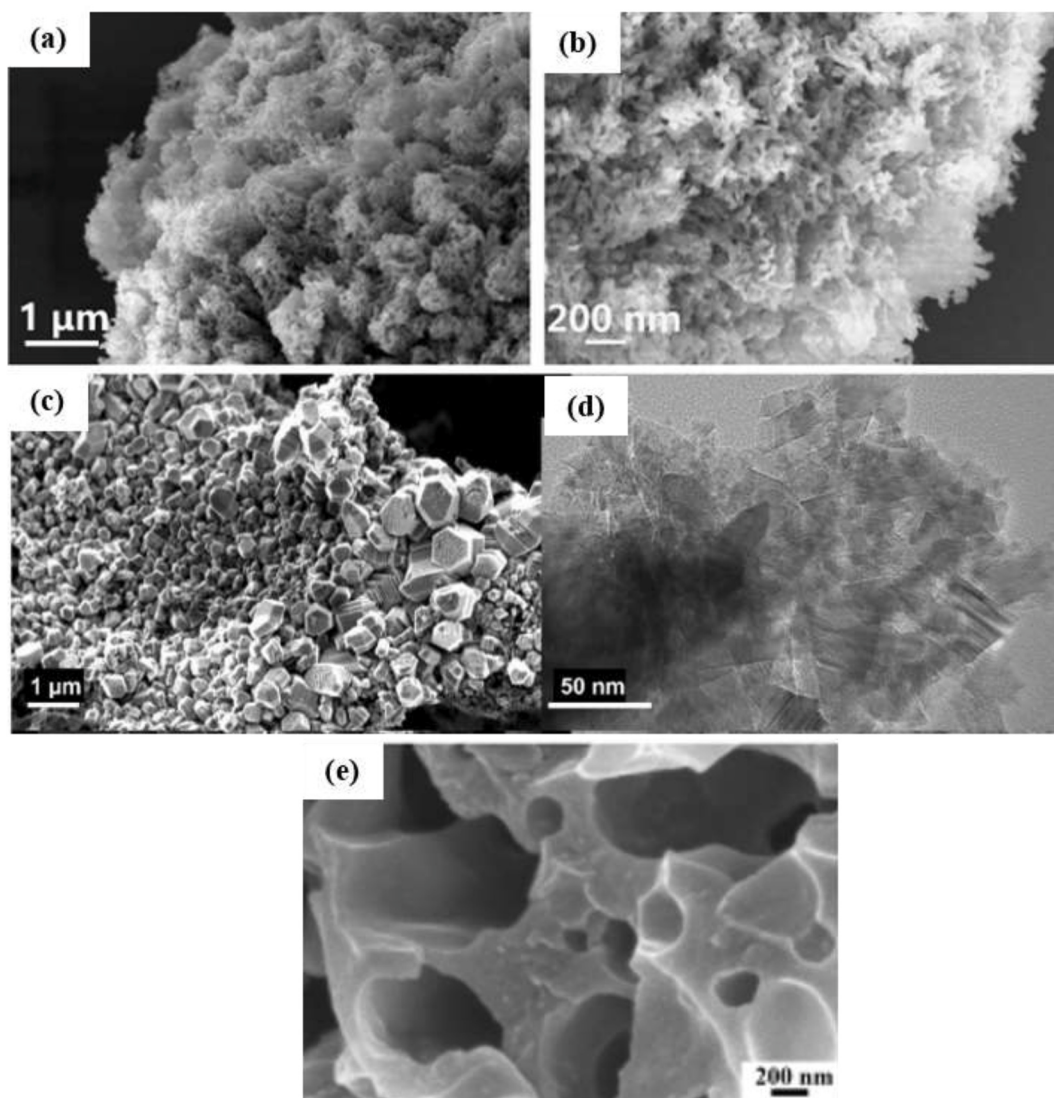
The reduction of silica to silicon is mostly done with metallothermic reactions which involve the conversion of metal or non-metal oxides, halides and sulfides into metal or non-metals, composites and alloys [12]. In the metallothermic reaction, reactive metals like calcium, aluminium, magnesium, potassium, sodium and lithium are often used as the reducing agent, which is “self-propagating exothermic reactions”. The metallothermic reaction process produced composites like  $\text{Li}_2\text{S}$ /transition metals [23], non-metals (such as carbon and silicon) and metals (such as vanadium, tantalum, niobium and titanium [24]. For instance, magnesium (Mg) is used to reduce silicon dioxide ( $\text{SiO}_2$ ) to elemental silicon (Si) and magnesium oxide (MgO) as represented in Equation (1). In this reaction, the reducing agent is magnesium while silicon dioxide ( $\text{SiO}_2$ ) is reduced to silicon (Si), and magnesium oxide (MgO) is formed as a by-product. The conventional technique is the carbothermal reduction process, which involves the extraction of silicon from silica by placing carbon and silica in an electric arc furnace and then heating up to 2000 °C [20]. Here, silicon dioxide is reduced to elemental silicon, and carbon is oxidized to form carbon monoxide (CO) as illustrated in Equation (2).

Magnesiothermic reduction is another method used for the production of silicon from silicon dioxide ( $\text{SiO}_2$ ) by reacting it with magnesium (Mg) at elevated temperatures usually above 1200 °C in argon or nitrogen atmosphere [25]. In this process, magnesium acts as the reducing agent, and the reaction is represented in Equation (3). Liu et al. [26] successfully reduced silica to silicon using a magnesiothermic technique without any impurity as shown in Fig. 1 (a) and (b). Haluska et al. [27] reduced silica derived from barley husks to silicon via magnesiothermic reduction. From both TEM and SEM images in Fig. 1 (c) and (d), the process led to a hexagonal-like layered structure while the particle size was below 50 nm.

For the aluminothermic reduction process, the process is used in the production of metals and alloys by the exothermic reaction between aluminium (Al) and a metal oxide. In the context of silicon production, the reduction process involves the reaction of silicon dioxide ( $\text{SiO}_2$ ) with aluminium to produce elemental silicon (Si) and aluminium oxide ( $\text{Al}_2\text{O}_3$ ) (see Equation (4)). The aluminothermic reduction process is typically carried out in a crucible or a similar container at high temperatures, often facilitated by the use of a starter mixture or an ignition source to initiate the reaction. The exothermic reaction provides the necessary heat for the process to proceed, and the products can be separated and refined as needed. Chen et al. [28] used aluminothermic methods successfully to reduce silica to silicon which resulted in a loosely porous structure and rough surface as illustrated in Fig. 1(e).



Out of all the reduction processes, the production of silicon by carbothermal reduction is an energy-intensive process due to the high temperatures required, but it remains a significant method for silicon production due to its effectiveness and scalability. One of the advantages of the magnesiothermic reduction process is that it can be carried out using relatively simple equipment and does not require the use of specialized furnaces [29]. However, the process may have limitations in terms of yield, purity, and scalability



**Fig. 1.** (a&b) SEM images of p-Si produced via the Magnesiothermic method from Liu et al. [26] (c) SEM images (d) TEM images of Si/C from Haluska et al. [27] (e) SEM image of Si reduced via aluminothermic method from Chen et al. [28].

compared to other methods such as carbothermal reduction. One of the challenges associated with the aluminothermic reduction process for silicon production is ensuring high purity and yield, as well as managing the reaction conditions to minimize the formation of undesirable by-products or impurities.

### 2.3. Economic aspect of extracting Si from agricultural wastes

Weighing the economic aspects of silicon (Si) extraction from agricultural wastes against Si obtained from direct minerals, there are several important factors to take into account, and the factors include:

**Costs of raw material:** Agricultural wastes such as sugarcane bagasse or rice husks are often free or inexpensive as they are by-products of agricultural processes. For instance, Goodman [30] stated that “rice husk is easily collected and cheap, so it has always had some use as an energy source for small applications”. In contrast, direct extracted Si involves mining and processing of quartz or other minerals which incurs expenses for things like processing, shipping and mining fees.

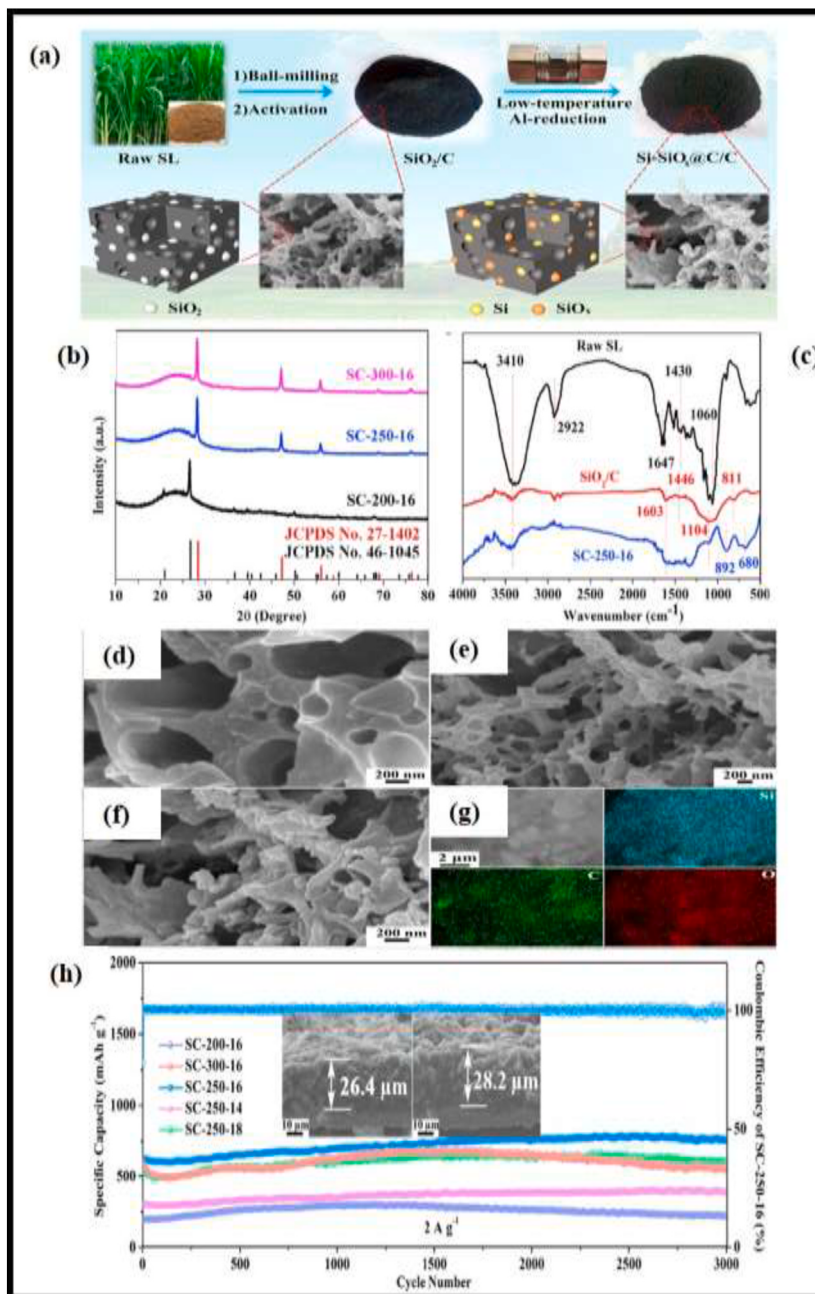
**Processing costs:** processing agro-waste into silicon precursors requires certain technologies such as hydrothermal treatment or pyrolysis treatment which have associated operational and capital costs. While directly extracted Si undergoes purification processes like refining and smelting [31] which might have different cost structures. For the two processes, the energy consumption and efficiency of these processes affect the cost. The efficiency and yield of silicon extraction from agro-waste and mineral extraction techniques affect the overall cost. Hence, processes involving agro-waste might require more purification stages or have lower extraction

yields which would reduce overall efficiency and cost effectiveness.

**Energy consumption:** One major cost component in processing is energy consumption. Smelting and refining are two energy-intensive steps in the direct extraction of silicon from minerals. Even though they could save money by employing waste heat or renewable energy sources, agricultural waste operations might still need energy.

**Labour cost:** The labour cost for fabricating composites and turning agricultural wastes into Si precursors may be different from those for extracting and processing minerals. The total cost of production can be affected by variables including labour intensity, skill needs and labour market circumstances.

In summary, as a result of lower raw material costs and environmental benefits, silicon derived from agro-waste may prove to be more cost-effective than silicon that is extracted directly. However, the total cost of production for Si/C composites will vary



**Fig. 2.** (a) Schematic illustration for the production of 3D porous Si-SiO<sub>2</sub>@C/C materials (b) XRD patterns of 3D porous Si-SiO<sub>2</sub>@C/C materials (c) FTIR spectra of 3D porous Si-SiO<sub>2</sub>@C/C materials; SEM image of (d) sugarcane leave (e) SiO<sub>2</sub>/C (f) SC-250-16 (g) elemental mapping images; (h) cyclic performance of the 3D porous Si-SiO<sub>2</sub>@C/C materials from Chen et al. [28].

**Table 1**

Agro-waste derived Si/C anodes materials for LIBs.

| Materials                        | Agro waste source                   | Mass of mixed materials                                                                                                     | Extraction Process                                                                    | Morphology                              | Surface area of Si/C composite (m <sup>2</sup> /g) | “Electrochemical performance (Initial Coulombic Efficiency, Charge Capacity/Discharge Capacity, cycling stability)”                                                               | Reference              |
|----------------------------------|-------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-----------------------------------------|----------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|
| Si/C nanocomposites              | Barley husks                        | Active material (80 wt%) of the active material; conductive agent (10 wt%); binder (10 wt %)                                | Annealed at 550 °C and Magnesiothermic reduction process; heated up to 2400 °C        | Hexagonal-like layered structure        | 196–272                                            | 67 ± 2 %; 294 ± 6 mAh g <sup>-1</sup> over 175 cycles                                                                                                                             | Haluska et al. [27]    |
| Si/C                             | Rice husk                           | Active material (60 wt%); binder (20 wt%); conducting carbon (20 wt%)                                                       | Microwave heating from 400 to 900 °C                                                  | Nanoparticles                           | –                                                  | 85 %; 600 mAhg <sup>-1</sup> over 200 cycles at 0.2 A g <sup>-1</sup>                                                                                                             | Gautam et al. [38]     |
| Si@SiOx                          | Waste coffee grounds and Rice husks | –                                                                                                                           | Leached with HCL, Calcination (900 °C for 2 h) and Magnesiothermic reduction process  | Nanoscale                               | –                                                  | 80 %; 1125 mAhg <sup>-1</sup> at 100 mA g <sup>-1</sup> after 100 cycles                                                                                                          | Liu et al. [26]        |
| Si/C                             | Rice husk                           | –                                                                                                                           | Zincothermic reduction                                                                | Nanoparticles                           | –                                                  | 1033 mAhg <sup>-1</sup> under 1 Ag <sup>-1</sup> after 100 cycles with 6.6 % capacity loss<br>745 mAhg <sup>-1</sup> under 2 Ag <sup>-1</sup> after 250 cycles                    | Zhao et al. [39]       |
| SiC/HC, Si/C                     | Rice husk                           | SiC/HC or SiC/O (70 wt %), C65 (20 wt %), and poly(vinylidene fluoride) (PVDF) binder (10 wt %)                             | Carbothermal reduction, heated at 1450 °C for 8 h                                     | Nanoporous                              | 42                                                 | 25 %; 950 mAh g <sup>-1</sup> after 600 cycles                                                                                                                                    | Yu et al. [40]         |
| Si-SiO <sub>x</sub> @C/C         | Sugarcane leaves                    | 70 wt% Si-SiO <sub>x</sub> @C/C; (70 wt %), acetylene black (20 wt%); sodium alginates (10 wt%)                             | Leached with HCL, Calcination (550 °C for 2 h) and aluminothermic reduction process   | 3D porous nanoparticles                 | 709                                                | 99.4 %; 1562.8 mAhg <sup>-1</sup> at 200 mA g <sup>-1</sup> after 400 cycles<br>49 %; 678.6 mAhg <sup>-1</sup> at 2 Ag <sup>-1</sup> after 3000 cycles                            | Chen et al. [28]       |
| Si/C                             | Rice husk                           | 60 wt% of activated material; 20 wt% of acetylene black; 20 wt% of binder                                                   | Heated at 700 °C for 3 h, leached with HCL and Magnesiothermic reduction process      | Nanoparticles                           | 27.47                                              | 92.4 %; 1247.8 mAh g <sup>-1</sup> over 50 cycles <sup>1</sup> at 100 mA g <sup>-1</sup>                                                                                          | Liao et al. [41]       |
| Si/C                             | Reed leaves                         | Active materials (60 wt %); sodium carboxymethyl cellulose (10 wt %); Super P (20 wt %); styrene butadiene rubber (10 wt %) | Heated at 750 °C for 8 h; Magnesiothermic reduction process; leached with HCL         | Hollow nanoparticles                    | 343.9                                              | 96 %; 650 mAhg <sup>-1</sup> at 500 mA g <sup>-1</sup> and 1548 mAhg <sup>-1</sup> at 100 mA g <sup>-1</sup> after 200 cycles                                                     | Wang et al. [42]       |
| Si/C                             | Rice husk                           | –                                                                                                                           | Heated at 900 °C; Magnesiothermic reduction process                                   | nanoparticles                           | –                                                  | 90 %; 420.7 mAhg <sup>-1</sup> and 540.3 mAhg <sup>-1</sup> at the rate of 0.2 Ag <sup>-1</sup> and 3 Ag <sup>-1</sup> after 150 cycles                                           | Ma et al. [19]         |
| (SiO <sub>2</sub> /C) and (Si/C) | Rice husk                           | Active Material (60 wt%); super-P (20 wt%); sodium alginate (SA) (20 wt%)                                                   | Leached with HCL, Calcination (800 °C for 3 h) and Magnesiothermic reduction process  | Nanoparticles with plate-like structure | –                                                  | SiO <sub>2</sub> /C:<br>40 %; 733 mAhg <sup>-1</sup> at 100 mA g <sup>-1</sup> after 50 cycles<br>Si/C:<br>49 %; 862 mAhg <sup>-1</sup> at 100 mA g <sup>-1</sup> after 50 cycles | Autthawong et al. [43] |
| Si/C                             | Rice husk                           | Si/C (70 wt%); acetylene black (15 wt%); sodium alginate (SA) (15 wt%)                                                      | Thermally treated at 600 °C for 2 h, leached HCL and aluminothermic reduction process | Mesoporous                              | –                                                  | 65 %; 460 mAhg <sup>-1</sup> after 300 cycles at 500 mA g <sup>-1</sup>                                                                                                           | Majeed et al. [36]     |

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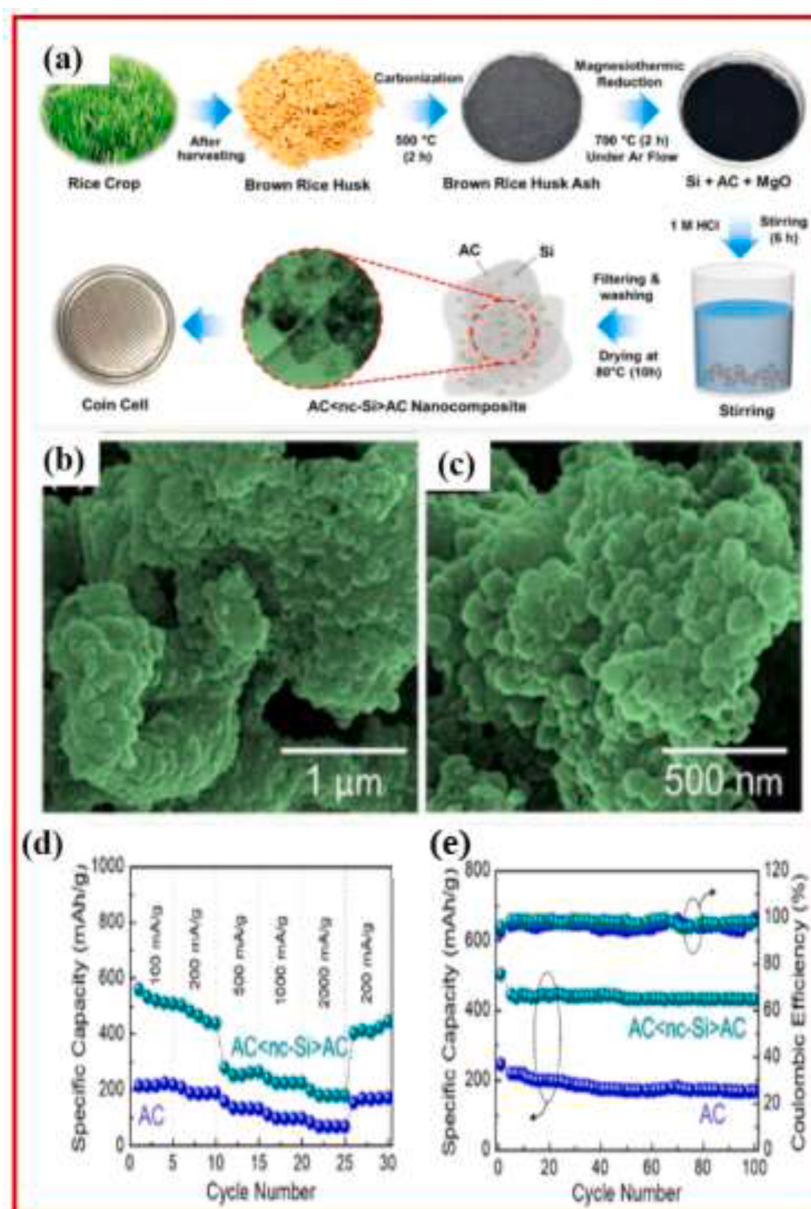
Table 1 (continued)

| Materials                                            | Agro waste source | Mass of mixed materials                                                                                                   | Extraction Process                                                                       | Morphology                                                                                                                                                                 | Surface area of Si/C composite (m <sup>2</sup> /g) | “Electrochemical performance (Initial Coulombic Efficiency, Charge Capacity/Discharge Capacity, cycling stability”                                                        | Reference                 |
|------------------------------------------------------|-------------------|---------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------|
| Si/C                                                 | Barley straw      | 7 active material (70 wt%); sodium-alginate (20 wt%); binder (10 wt%)                                                     | Thermally treated at 1000, 1400, 1800, 2000, 2200 and 2400 °C                            | 1000 °C: spherical shape and size<br>1400 °C: nano-sized SiC (1800–2200 °C): particle fusion and agglomerate growth<br>2400 °C: hollow graphite shells and graphite flakes | –                                                  | At 1000 °C: 38 %, 1180 mAhg <sup>−1</sup> at 0.1 Ag <sup>−1</sup>                                                                                                         | Meščeriakovas et al. [44] |
| Activated-C-decorated Si nanocrystals                | Rice husk         | Three different active materials (80 wt%); Carbon black (10 wt %); polyvinylidene difluoride (10 wt%) m                   | An annealed at 500 °C for 2 h, leached with HCL and Magnesiothermic reduction process    | Nanosheet                                                                                                                                                                  | 498.5                                              | 97.5 %; 716 mAhg <sup>−1</sup> after 100 cycles at 429 mA g <sup>−1</sup>                                                                                                 | Sekar et al. [6]          |
| Si/C and SiO <sub>2</sub> /C nanocomposites          | Rice husk         | Active materials (70 wt%); P carbon black (15 wt%); polyvinylidene fluoride (PVDF, 15 wt%)                                | Heated at 700 °C for 6 h, leached with HCL and Magnesiothermic reduction process         | Nanoparticle structures                                                                                                                                                    | –                                                  | 61.93 %; 650 mAh g <sup>−1</sup> at 100 mA g <sup>−1</sup> after 150 cycles                                                                                               | Chu et al. [45]           |
| 3D structured Si/C                                   | Rice husk         | –                                                                                                                         | Magnesiothermic reduction process                                                        | 3D nano-porous                                                                                                                                                             | 198.79                                             | 49 %; 537 mAhg <sup>−1</sup> after 200 cycles at a current density of 0.1 A g <sup>−1</sup>                                                                               | Yu et al. [46]            |
| Si@N-doped Carbon                                    | Horsetail         | Si@N–C materials (60 wt%), super P (30 wt%); sodium alga acid (CMC) (10 wt%)                                              | Leached with HCL; thermally treated at 800 °C for 6 h; Magnesiothermic reduction process | Nanoscale particles                                                                                                                                                        | 173.7–273.59                                       | 60 %; 1047.1, 1148.8 mAhg <sup>−1</sup> at 0.5 Ag-1 after 450 cycles and 750 mAhg <sup>−1</sup> at 1 Ag <sup>−1</sup> after 760 cycles                                    | He et al. [22]            |
| Silicon/nitrogen-doped carbon/carbon nanotube (SNCC) | Rice husk         | Active material (65 wt %); super-P acetylene black (20 wt %); styrene-butadiene rubber/ carboxymethyl cellulose (15 wt %) | Leached with HCL; heated at 700 °C for 2 h; Magnesiothermic reduction process            | Nanotube                                                                                                                                                                   | 78.5                                               | 67 %; 1460 mAhg <sup>−1</sup> at 0.1 Ag <sup>−1</sup> , 1380 mAhg <sup>−1</sup> at 0.5 Ag <sup>−1</sup> and 978 mAhg <sup>−1</sup> at 1 Ag <sup>−1</sup> after 100 cycles | Zhang et al. [47]         |
| Si/C                                                 | Bamboo leaves     | –                                                                                                                         | The magnesiothermic reduction process then reduced at 650 °C                             | Irregular micro-sized particles with a rough surface                                                                                                                       | 201                                                | 60 %; 600 mAhg <sup>−1</sup> at 2 Ag-1 after 3700 cycles                                                                                                                  | Lin et al. [48]           |

depending on a number of factors, including labour costs, processing techniques, efficiency, energy consumption, and production scale. To determine the precise difference in manufacturing costs between the two systems, a thorough cost study taking these elements into account must be performed.

### 3. Si/C composite anodes derived from agro wastes for LIBs

Silicon undergoes significant volume expansion ( $\sim 300\%$ ) upon lithiation, leading to mechanical stress, electrode pulverisation, and eventual degradation of the battery performance. The volume expansion can cause electrode cracking, loss of electrical contact, and increased impedance, thereby compromising the cycling stability and overall lifespan of the battery. The repeated contraction and expansion of the silicon particles during charge-discharge cycles can result in the creation of an unstable solid-electrolyte interface (SEI) layer, leading to capacity fading and reduced coulombic efficiency. Maintaining structural integrity and mitigating degradation mechanisms are crucial for achieving long-term cycling stability and reliable battery performance [9,10]. Nevertheless, a workable solution to the problems associated with using silicon as an anode material in lithium-ion batteries is to combine silicon derived from



**Fig. 3.** (a) Schematic diagram of developed Si/C nanocomposite derived from Brown rice husk (b & c) SEM image of the developed composite material (d) Coulombic efficiency and (e) Specific capacity of the sample from Sekar et al. [6]

agro-waste with carbon-based materials. The addition of carbon, improves the total conductivity of the composite, enabling more effective electron movement throughout the charge-discharge cycle. Also, carbon materials mitigate the volume expansion problems linked to pure silicon which reduces the mechanical stress and improves the anode's cycle stability [12]. The sources of carbon in the composite could be derived from external sources or Si.

Usually, the external sources of carbon in Si/C composite include organic polymers [32], and carbonaceous materials like graphene [33], carbon nanotubes [34] and graphite [35]. For example, Wang et al. [20] developed Si/C nanoparticles using scalable techniques. At first, the silicon nanoparticles are derived from bamboo leaves starting with thermal decomposition and then following with a magnesiothermic reduction process. To improve the Si anode properties, it is then coated with "Reduced Graphene Oxide (RGO)" and a thin amorphous carbon layer to fabricate "Si@C/RGO nanocomposite for high-performance lithium-ion battery". The inclusion of RGO and the amorphous carbon provides dual protection, by reducing volume fluctuations, upsurging electrical conductivity, preventing direct contact between the silicon and electrolyte which ultimately boosts the battery performance. The findings from Wang et al. [20] show that preparing Si/C nanocomposite from agro-waste is more cost-effective and straightforward when compared with using other external sources.

Majeed et al. [36] produced Si/C anode utilizing low-cost rice husk as the source of silicon for LIBs applications. Extraction of  $\text{SiO}_2$  from rice husk (RH) was done using the leaching process then the  $\text{SiO}_2$  was reduced to Si using aluminothermic reduction. The XRD pattern had a semi-crystalline feature (the combination of amorphous and crystalline features) with several sharp peaks which indicates the effectiveness of the aluminothermic reduction process. The Si/C anode thermogravimetric analysis (TGA) curve is presented. The TGA curve shows a slight weight loss below 370 °C then followed by a sharp weight loss within 370–580 °C attributed to the elimination of carbon material from the composite. The SEM image had some small particles (Si) dispersed randomly around the bigger one (C) and it confirmed that the Si particles are attached to the surface of the carbon. Also, the proper dispersion shows a good contact which benefits the transfer of charge between the carbon and Si particles. Both the carbon matrix and the particles connected to the reduction of silica ( $\text{SiO}_2$ ) into Si and the calcination of RH exhibit certain irregular pores. The separated Si particles may be connected by the porous carbon matrix serving as a bridge. The Si/C anode exhibited good electrochemical performance ascribed to the addition of carbon which minimises side reactions, generates effective bicontinuous conductive channels and preserves structural stability by permitting volume fluctuation [37].

A molten-assisted low-temperature aluminothermic reaction was introduced by Chen et al. [28] to produce a "3D porous carbon network embedded Si- $\text{SiO}_x$ @C/C" composite. The sources of carbon and silica are sugarcane leaves while the preparation process is shown in Fig. 2(a). The aluminothermic reaction was used to reduce the silica derived from sugarcane leaves to silicon, the effect of different aluminothermic reduction times and temperatures (250 °C for 18 h, 250 °C for 14 h, 300 °C for 16 h and 200 °C for 16 h labelled as SC-250-18, SC250-14, SC-300-16 and SC-200-16). From the XRD patterns in Fig. 2(b), the aluminothermic reduction shows the reduction from silica to silicon can take place between 250 and 300 °C. Increasing aluminothermic reaction time increased the intensity of Si peak and impure peaks were seen. For the FTIR spectra, the asymmetric  $\text{SiO}_4$  tetrahedral ring and Si–O–Si stretching vibration were seen at about 811 and 1104  $\text{cm}^{-1}$  respectively presented in the SC-250-16 sample and the  $\text{SiO}_2$ /C precursor (see Fig. 2(c)). The SEM image before the reduction process was characterized by a fluffy and rough surface (see Fig. 2(d)). After the reduction process, a loosely porous structure was seen in Fig. 2 (e&f) while Fig. 2(g) shows a uniform distribution of the constituents. Fig. 2(h) indicates that the sample produced at 250 °C for 16 h possesses excellent cycling stability and it is then recommended for application for real application. Therefore, taking into account its economic worth and eco-friendly features, developing Si/C anode from agro-waste seems to be the most dependable option for the future. Innovative synthesis techniques are still in great need, nevertheless, as there is still a significant gulf between existing technology and real-world industrial use. Table 1 presents the summary of several silicon-based materials that are generated from agro-waste used as LIB anodes.

Also, Sekar et al. [6] developed Si/C nanocomposite ( $\text{AC} < \text{nc-Si} > \text{AC}$ ) from brown rice husk through "a single-step simultaneous synthesis method". The collected rice husk was first thermally treated at 500 °C in air for 2 h. Magnesiothermic reduction was done on the samples as illustrated in Fig. 3(a). The SEM image in Fig. 3(b&c) shows that there is a lot of combined structure of spherical nanoparticles which fall within 40–60 nm diameter. Due to the synergistic benefits derived from silicon nanocrystals (such as low discharge potential and high specific capacity) and activated carbon (including high porosity and excellent electrical conductivity), the Si/C nanocomposites demonstrate significant potential as an anode material for lithium-ion batteries (LIBs). Specifically, they exhibit notable characteristics such as a remarkable coulombic efficiency (97.5 %), a substantial discharge capacity (716 mAh/g), and a notable reversible specific capacity (429 mAh/g after 100 cycles) when employed as a LIB anode (see Fig. 3(d) & e).

#### 4. Preparation of Si/C composites anodes for LIBs applications

Developing Si/C composite involves Si sources (i.e., Si oxide, Si powder, liquid or gaseous compounds of Si) and carbon sources (i.e., organic compounds like pitch and toluene) or polymeric materials such as polyacrylic acid (PAA) or polyvinyl alcohol (PVA). The synthetic techniques used to obtain the Si/C include pyrolysis, hydrothermal, mechanical ball milling, spray drying, chemical vapour deposition (CVD) and other methods.

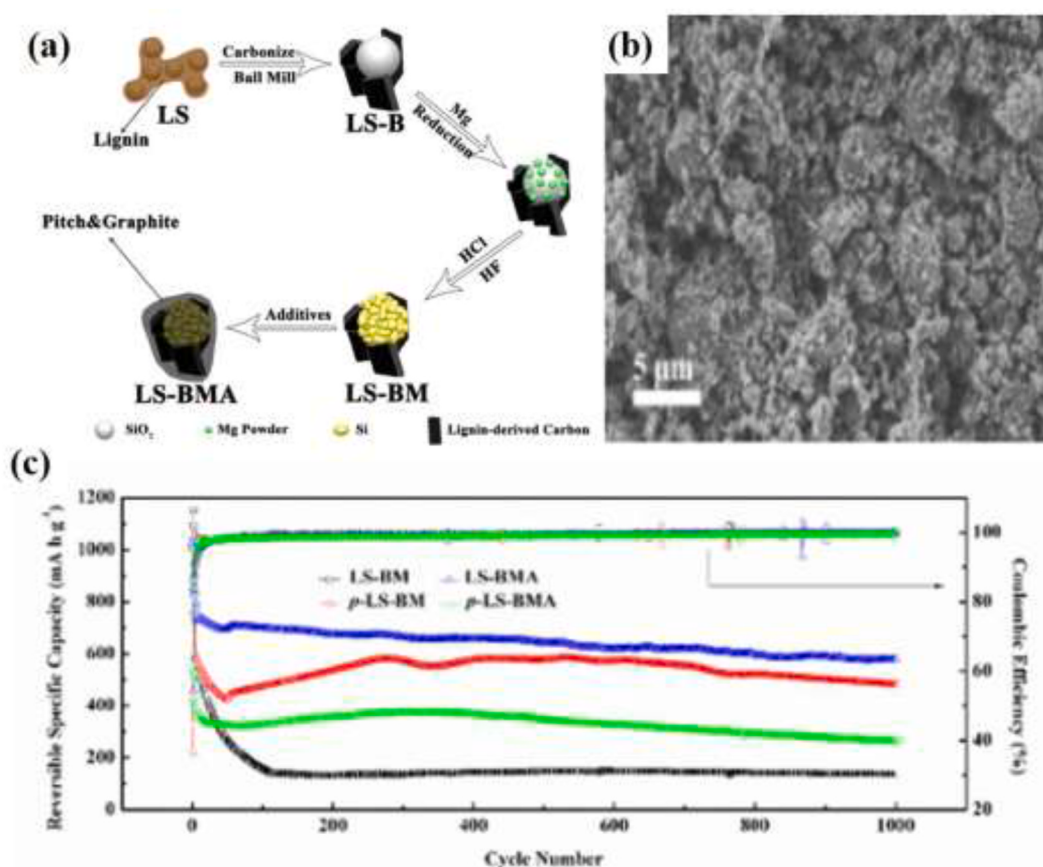
##### 4.1. Mechanical ball milling

This technique is used to grind raw materials into fine powders using a rotating chamber and balls. The ball milling process helps in achieving homogenous mixing of the silicon and carbon components, which is crucial for the performance of the anode material. During milling, the mechanical energy provided by the milling balls leads to the breaking and blending of the materials at the

nanoscale, resulting in a uniform distribution of silicon within the carbon matrix. The anode material's performance depends on the silicon and carbon components being mixed uniformly, which is made possible by the ball milling process [49,50]. Homogeneous distribution of silicon inside the carbon matrix is the ultimate consequence of the breaking and mixing of the materials at the nanoscale caused by the mechanical energy generated by the milling balls. Ball milling techniques aid in refining the particle size, reduce the activation energy reaction, induce chemical reactions resulting in the synthesis of new compounds and materials and improve the particle activity. This technique is widely utilized in various industries, including materials science, pharmaceuticals, and electronics, among others. In the production of Si/C composite for LIBs applications, this technique is used as a standalone or in combination with other methods.

For instance, Zhao et al. [51] developed "SiC-free C-S alloys by the delithiation of ball-milled C-Li-Si alloys". The powder of Li<sub>12</sub>Si<sub>7</sub> was milled with graphite in a 65-mL hardened steel enclosed with stainless steel balls. The authors observed that direct milling of Si and C products led to pronounced SiC XRD peaks which indicate the nanocrystalline SiC phase. Also, the milling process for the production of Si/C electrodes gave stable cycling performance, high reversible capacity and low volume expansion. Similarly, Parekh et al. [52] produced a double carbon-coated silicon anode by milling the nanoparticles for 20 min at 15 Hz. The synthesis enhances the structural stability and also improves the electrochemical kinetics properties of the composite. The ball milling production process involves either a dry or wet milling process. Cabello et al. [53] produced a high-power SiC anode via a wet ball milling process. The process was conducted using 10 mL of IPA for 10 min at 1000 rpm. The mechanical ball milling process is used alone or in combination with other preparation techniques. For instance, Han et al. [54] produced a Si/C composite through the ball milling method then followed by pyrolysis using deionized water and PVP. Mechanical milling technique has been used for producing Si/C composite from agro-waste. For instance, Li et al. [55] developed a Si/C composite from rice husk through balling-milling at 800 rpm for 6 h (see Fig. 4 (a)). A comparison was made between samples made through ball-milling with and without carbonization. The resulting product shows that the ball-milling process made the carbon coating more visible as shown in Fig. 4(b) and outstanding electrochemical properties were seen as illustrated in Fig. 4(c) which shows improved cycling performance and specific capacity.

The primary feature of mechanical ball milling is the way mechanically enhanced forces alter the physicochemical and structural characteristics of Si/C particles, opening up new possibilities for nanostructure creation. Ball milling is a practical, affordable, and simple process for producing Si/C materials in large quantities, but because the particles are broken down randomly by the machine,



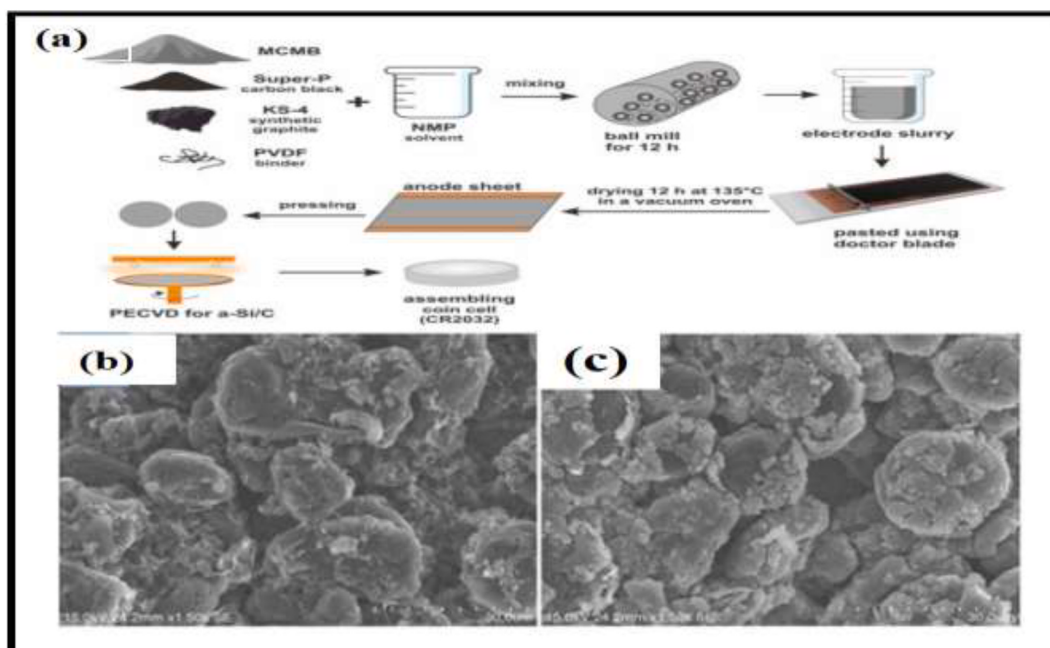
**Fig. 4.** (a) Schematic illustration of Si/C composite made from ball-milling technique (b) SEM image (c) cycling performance of the developed composite through balling milling from Li et al. [55].

there are still issues with the end products' purity and particle size distribution [56]. Ball milling is frequently more economical as compared to some alternative synthesis techniques like chemical vapour deposition (CVD) or sol-gel procedures. Lower manufacturing costs are achieved by using less complex equipment and fewer processing processes [57]. Also, compared to other synthesis processes, ball milling has a lower environmental effect since it usually does not need the use of harsh chemicals or high temperatures. For this reason, it is widely regarded as an ecologically benign procedure.

#### 4.2. Chemical vapour deposition

In materials science and engineering, chemical vapour deposition (CVD) is a commonly used method for developing high-quality, high-performance thin films and coatings. Si/C composites are desirable options for high-performance lithium-ion batteries because of their strong conductivity and large theoretical capacity. The process involves the thin film deposition on a substrate by introducing volatile precursor gases into a reaction chamber where they undergo chemical reactions and deposit as a solid material on the substrate. In the production of Si/C for LIBs application, the technique involves depositing a carbon layer and silicon layer on substrate materials using carbon sources (i.e., toluene) and Si sources (i.e., silane) [56,58,59]. This technique has not been used widely in the production of Si/C composite from agricultural waste. However, the CVD can be employed to deposit silicon (Si) and carbon (C) onto a substrate, which may be derived from agro-waste such as rice husks, sugarcane bagasse, or other biomass sources. Several studies have produced Si/C composite via chemical vapour deposition. For instance, Suresh et al. [60] synthesized Si/C nanoparticles using chemical vapour deposition at 1150 °C. It was observed that the buffering function between the graphite and CNM protective layers on Gr-Si-CNM functions to lessen the direct interaction between the Si film and the electrolyte, so inhibiting the production of SEI inside the Si. Zhang et al. [61] prepared Si/C nanospheres through the CVD technique at 900 °C. the produced nanosphere had diameters between 400 and 600 nm while the main constituent were Si and C. It was observed that the CVD technique resulted in a consistent distribution of C and Si.

The chemical vapour deposition can be combined with other preparation techniques. For instance, Lee et al. [62] developed “a commercial carbonaceous anode” with a-Si layers through ball milling and chemical vapour deposition technique for LIBs applications (see Fig. 5(a)). The SEM image shows that the carbon anode is covered with Si surface while the flake graphite edges became blurred. The morphology of the developed Si/C was studied with 960 and 640 nm layers of Si after 30 cycles as illustrated in Fig. 5(b&c), and the SEM image had no large volumetric strain that might led to mechanical damage. However, localized cracks could be seen in the image. The benefit of the CVD process is that a variety of avirous-structured Si/C materials may be coated on various silicon or carbon substrates to improve performance and it is a capable avenue for future research. Large-scale manufacturing of Si/C materials is not feasible using this method due to its high cost, high energy consumption, low efficiency of Si/C materials produced by CVD, and risk and pollution associated with the reaction process [56]. The process of refining the deposition parameters to produce coatings with the appropriate thickness, shape, and content. The electrochemical performance of the resultant anodes is directly impacted by the homogeneity and consistency of the coatings, which are ensured by careful control over the deposition process.



**Fig. 5.** (a) Schematic illustration of C Anode with a-Si Layers produced via CVD; SEM image of Si/C after charge-discharge test after 30 cycles (b) 960 nm layer of Si and (c) 640 nm layer of Si from Lee et al. [62].

### 4.3. High-temperature pyrolysis

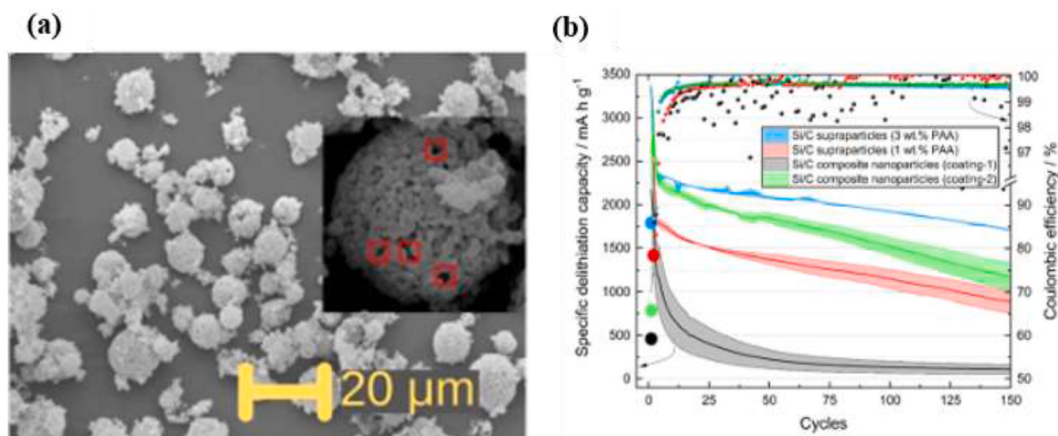
The thermal breakdown of organic or inorganic materials at high temperatures without oxygen (or under-regulated oxygen conditions) to create volatile chemicals, gases, and solid leftovers is known as high-temperature pyrolysis. This procedure is essential for the synthesis of innovative materials, the creation of energy, and the treatment of waste in many fields, including environmental science, chemistry, and materials science. Si/C anodes are generally produced via high-temperature pyrolysis which involves transforming polymers into amorphous carbon in an inert atmosphere [56]. Higher temperature pyrolysis of polymers produces amorphous carbon with a more abundant pore structure that is better able to withstand volume changes in Si-based materials and functions as an external buffer for silicon materials [63]. In order to create the appropriate Si/C composite material, high-temperature pyrolysis involves heating Si/C precursors to temperatures that are often higher than 600 °C in an inert environment. This causes molecular structures to break down and reorganise. Without requiring a deposition stage, this approach enables the direct conversion of precursor elements into the required composition [64,65].

Nyamtara et al. [66] utilized “a two-step pyrolysis synthesis method to make a carbon-coated silicon nanoparticle composite”. Coal tar was the carbon source and recycled industrial solar cells were the sources for silicon nanoparticles. The SEM image of the developed Si/C composite had different particle sizes, an irregular and angular-shaped morphology. It demonstrated an average coulombic efficiency of 99.8 %, a high discharge capacity of 1524 mAhg<sup>-1</sup>, and a discharge capacity retention of 75.7 %. High-temperature pyrolysis has been used to produce Si/C composite from agro-waste. For instance, Wang et al. [64] developed a nanoporous Si/C composite via high-temperature pyrolysis using rice husks and CO<sub>2</sub> as silicon and carbon sources respectively. The mixture of SiO<sub>2</sub> and Mg powder was done in a corundum reactor then calcined at 680 °C in a tube furnace and CO<sub>2</sub> flowed through an open corundum reactor.

All things considered, high-temperature pyrolysis presents a viable method for turning organic resources into useful products, aiding in the creation of ecologically beneficial and sustainable technology. The ease and scalability of high-temperature pyrolysis is one of its benefits. The procedure, which entails heating the precursor mixture in an appropriate reactor under carefully monitored circumstances, can be very simple. Because of this, it can be used to produce Si/C composites on a massive scale. Furthermore, by varying variables like precursor composition, heating rate, and pyrolysis temperature, high-temperature pyrolysis provides flexibility in modifying the composition and characteristics of the resultant Si/C composites. Because of its adaptability, the material's electrochemical performance including its capacity, cycle stability, and rate capability can be optimised to satisfy particular battery needs [67,68].

### 4.4. Spray drying

A flexible method for creating anodes for lithium-ion batteries is spray drying Si/C composites. Spray drying is one method that may be used to create composite powders that mix silicon (Si) and carbon (C) components for use in Si/C anode materials for LIBs. The solution includes binders, solvents, carbon compounds (such as graphene or carbon black), and silicon nanoparticles or microparticles. It has the benefit of fine control over the composition, shape, and scalability of the particles [69]. Spray drying is a method for producing powdered materials and the materials to be dried are broken up into tiny particles, similar to fog, by mechanical action and then come in contact with heated air [70]. During the spray drying process, the silicon and carbon materials can be homogeneously mixed at the particle level, resulting in a composite structure. While silicon adds to high capacity and performance, carbon helps to increase the anode material's mechanical stability and electrical conductivity. Due to the advantages, more researchers are using this method to produce Si/C anode composite. For instance, Zhou et al. [71] developed “silicon/graphite/polydopamine derived carbon derived” by two-step heat treatment and spray drying process. A solution was made from the continuous stirring of silicon powder,



**Fig. 6.** (a) SEM image of the produced Si/C composite after spray drying (b) Average Coulombic efficiency and specific delithiation capacity of the composite from Amin et al. [72].

graphite, alcohol, citric acid and deionized water. The homogeneous solution was spray-dried using dry air which resulted in a solid precursor. The result shows that the developed sample still keeps its inherent crystalline structure after the heat treatment and spray drying process.

A one-step non-reactive spray dry technique was developed by Amin et al. [72] to produce Si/C composite nanoparticles for LIBs applications. It was observed that the spray drying process led to supra particles and a unique structure made of rich silicon and spherical morphology of carbon (see Fig. 6(a)). The supraparticles of the produced composite led to 86 % Coulombic efficiency and excellent cycling stability after the first cycle while 80 % was seen after the third cycle and 65.2 % after 126 cycles as shown in Fig. 6 (b). In summary, spray drying is a viable method for producing Si/C composite anode materials with tailored properties for high-performance LIBs.

Few studies have reported using spray drying methods for producing Si/C composite for LiB applications. Xu et al. [73] developed watermelon-inspired Si/C microspheres via spray drying and CVD process. From the SEM in Fig. 7(a), the produced sample is dispersed homogeneously with a more compacted Si/C structure and the grain size is properly distributed. After several cycles, the densely compacted Si/C composite produced via the spray drying process gave 89.2 % initial coulombic efficiency and 99.8 % average coulombic efficiency (see Fig. 7(b)). Research and development efforts continue to focus on optimizing this process and exploring novel material formulations to further enhance battery performance and durability. When compared to other techniques, the size, shape, and morphology of the resultant particles may be precisely controlled during the spray drying process, which can have an impact on the anode material's electrochemical performance. Also, Spray drying makes it easier for the silicon and carbon precursors to combine uniformly and evenly throughout the final composite particles by dispersing the precursor components in a liquid solution before atomization [74,75].

#### 4.5. Hydrothermal synthesis

Materials can be synthesized using the hydrothermal synthesis approach in an aqueous environment under high pressure and temperature. Hydrothermal synthesis may be used to create composite materials with improved characteristics when it comes to Si/C anode materials for LIBs [56]. The solution comprises Si nanoparticles, carbon sources and other binders or additives and the solution is enclosed in a reactor at high pressure at a certain time at regulated temperatures (100 °C and 300 °C). Through chemical reactions and phase transitions, the hydrothermal environment facilitates the production of Si/C composite materials. While the silicon precursors react to generate silicon nanoparticles or clusters dispersed within the carbon matrix, the carbon precursors break down and polymerize to form a carbon matrix during hydrothermal treatment. The degree of silicon carbonization and crystallisation, as well as the shape and characteristics of the resultant Si/C composite, are all influenced by the length of time and temperature of the hydrothermal treatment. The Si/C composite materials may go through extra processing procedures including drying, washing, and heat treatment after hydrothermal synthesis to get rid of contaminants and leftover solvents while also improving the composite's qualities [76–78].

The hydrothermal process led to a homogenous composite structure since the silicon integrated easily into the carbon matrix due to the high temperature and pressure conditions. “Double-shell structured Si@SnO<sub>2</sub>@C nanocomposite” was produced by Lei et al. [79] via hydrothermal technique. The TEM image confirmed the double-shell structure while the layers of C and SnO<sub>2</sub> have thicknesses of 7 and 20 nm respectively. The electrode has a remarkable rate capability of 340 mAhg<sup>-1</sup> at 1500 mAg<sup>-1</sup>, as well as a high initial discharge capacity of 2777 mAhg<sup>-1</sup> at 100 mAg<sup>-1</sup> after 300 cycles and exceptional capacity retention is 50.2 %. To the best of our knowledge, no study has reported the use of hydrothermal synthesis for producing Si/C composite made from agro-waste. Overall, hydrothermal synthesis offers a versatile approach to producing Si/C composite materials with tunable properties, making them suitable for a wide range of applications. Similar to the spray dry technique, particle shape and size distribution may be manipulated by the hydrothermal process by adjusting reaction parameters including temperature, pressure, and reaction time. Also, Hydrothermal synthesis enables the homogenous mixing of silicon and carbon precursors by dissolving or dispersing the precursors in a solvent,

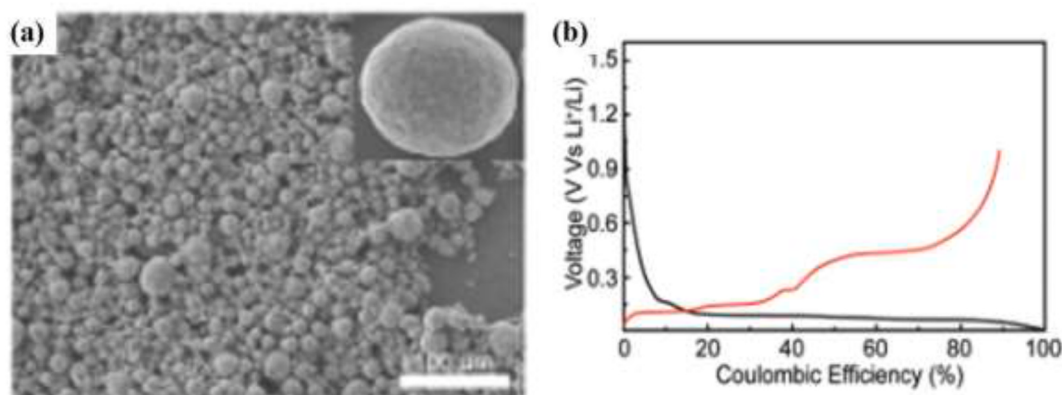


Fig. 7. (a) SEM image (b) Coulombic efficiency of the watermelon-inspired Si/C microspheres from Xu et al. [73].

resulting in uniform composition throughout the resultant composite particles. Water is a cheap, readily available, and ecologically benign solvent utilized in hydrothermal synthesis, as opposed to the organic solvents employed in other synthesis techniques [56].

#### 4.6. Other synthesis techniques

In addition to other techniques mentioned in the preceding sections, Si/C anode can be produced using magnetron sputtering, electrostatic spraying, centrifugal spinning and other techniques. When combined with other conventional methods, the synthesis method mentioned above led to strong adhesion between the two materials and also possessed high purity. However, the main drawback of the technique mentioned above is that it can not be used in producing Si/C composite in large quantities due to the cost associated and energy consumption. Hence, this limits its application in the industry [56]. Nava et al. [80] developed a Si/C fibre hybrid using the centrifugal spinning method at 6000 revolutions per minute. The authors studied the influence of uniform distribution of porous carbon and Si nanoparticles, on the electrochemical performance. The developed hybrid had excellent structural stability capacity of 952 mAh/g and 99 % Coulombic efficiency. Through using centrifugal spinning, the developed material had a porous and nanocrystalline structure. Also, it improves the volume expansion and surface area. Electrostatic spraying is another technique that can be developed for the making of Si/C composite materials. When fabricating Si/C composites, silicon-containing precursors can be deposited onto substrates via electrostatic spraying, and then the precursors can be carbonised to create the Si/C composites.

The electrostatic spray involves the use of an electric field that produces a large electron which guides the dispersion of carbon and silicon materials. Liang et al. [81] used electrostatic spray to develop a Si/C composite using Si particles and carbon nanotube sources. It was observed that the carbon layer protects the silicon nanoparticles from the electrolyte and aids in avoiding unstable SEI formation. In another article, Chen et al. [82] developed a “multichannel carbon fibre confining Si NPs composite” using the electrospinning-carbonization technique. By controlling the electrospinning and carbonization parameters, the electrospinning-carbonization method can be optimised to produce Si/C composites with desired properties for applications such as LIBs, energy storage devices, and high-temperature materials.

### 5. Challenges faced in preparing silicon–carbon composites anodes derived from agro wastes

Si/C preparation presents a number of difficulties. Although silicon has a high theoretical capacity, throughout the lithiation and delithiation cycles, it experiences large volume fluctuations that cause mechanical stress and, in the end, pulverisation of the electrode material. Here are some challenges faced in preparing silicon-carbon composite anodes derived from agro wastes:

- Volume Expansion

During lithiation, silicon experiences a large volume expansion of up to 300 per cent, which causes pulverisation and mechanical stress of the anode material. Cycle life may be shortened and electrode deterioration may occur from this.

- Cycle Stability

Maintaining long-term stability over multiple charge-discharge cycles is a significant challenge. The repeated contraction and expansion of the silicon particles can lead to electrode degradation and loss of capacity over time.

- Silicon Agglomeration

Agro waste-derived silicon particles may agglomerate during the fabrication process, leading to uneven distribution within the composite. This uneven distribution can result in localized stress concentrations and compromise the overall performance of the anode.

- Carbon Coating Uniformity

Achieving a uniform carbon coating on the silicon particles is crucial for enhancing electrical conductivity and mitigating the volume expansion issue. Inadequate or uneven carbon coating can lead to performance degradation.

- Agro Waste Processing

The efficient extraction and processing of silicon from agro-waste pose challenges. The selection of suitable agro-waste materials, optimization of extraction methods, and minimizing impurities are critical for obtaining high-quality silicon for the composite anode.

- Binder Selection

Choosing an appropriate binder is crucial for maintaining electrode integrity during the charge-discharge cycles. Silicon-carbon composites may require binders that can accommodate the volume changes and provide good adhesion to the current collector.

- Cost and Scalability

Ensuring the scalability and cost-effectiveness of the production process is essential for practical applications. The choice of agro-waste materials, processing methods, and the overall fabrication process must be economically viable on a large scale.

- Safety Concerns

Silicon anodes may be prone to the formation of a solid-electrolyte interphase (SEI) layer, affecting the performance and safety of the battery. Managing the formation of a stable SEI layer is a critical aspect of silicon anode design.

## 6. Potential solutions to the stated challenges

The possible solution to volume expansion of the composite materials is to design composite structures that can adapt to volume change over the cycles of lithiation and delithiation by using hierarchical design. Also, incorporating high-performance binders or flexible carbon matrices reduces mechanical stress and prevents structural deterioration. Taskin et al. [83] reported features of the binders for LiBs application to obtain desirable properties. It was reported that polar functional groups like  $-\text{CN}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{O}(\text{CO})\text{R}$ ,  $-\text{COOH}$ ,  $-\text{OH}$  etc. should be present in the binder material to encourage strong bonds between the particles which could maintain a charge percolation network. The binders should be non-hazardous, eco-friendly and low-cost. Also, the binder materials should be highly electrochemical stable, and they must be physically and chemically stable when in contact with an electrolyte.

On the cycle stability, this challenge can be overcome by developing strategies to mitigate electrode degradation and electrolyte breakdown such include protecting the composite's surface with protective layers or adjusting the electrolyte's composition. Several research works have reported coating the Si/C composite with different materials. For instance, Li et al. [84] developed a nano-silica/carbon composite and the surface of the silica nanoparticles was coated with resorcinol and formaldehyde using the copolymerization technique. The findings show the developed composite maintained a consistent capacity of approximately 620  $\text{mAhg}^{-1}$  at a current density of 100 mA per gram and the composite exhibited nearly 100 % capacity retention after 300 cycles. Optimizing temperature, pressure, heat treatment time, and the ratio of silicon to carbon precursors are just a few of the factors that must be optimised to develop an effective and scalable synthesis method for creating silicon-carbon composites from agricultural wastes. However, it can be difficult to strike the ideal balance between these variables to optimize the composite's electrochemical qualities while lowering production costs. To achieve uniformity and consistency while preventing silicon agglomeration, it is encouraged to employ method sonication or ball milling to ensure homogenous mixing of carbonaceous precursors with silicon particles. Several authors utilized the ball milling technique either as a standalone or combined with other techniques [50,51,85]. However, it is encouraged to optimize the mixing parameters and the use of surfactants which can help achieve uniformity and better dispersion within the composite.

To prevent the development of an extremely "unstable solid-electrolyte interphase (SEI)" layer caused by the loss of contact resulting from volume expansion, various approaches can be considered. For example, using carbons obtained from agro-waste, both soft and hard, which are plentiful in heteroatoms (showing higher surface activity) and functionalities, might improve the electrochemical performance in place of graphite. Moreover, biomass-derived carbons are easily modifiable through the introduction of heteroatoms and metal doping because of their enhanced surface activity. By putting these tactics into practice, the carbon-silicon's physicochemical and electrochemical stabilities can be improved (C@Si) [36]. An alternative approach involves blending diverse carbon forms, derived from various agro-waste precursors and synthesized through different methods, with silicon. This method aims to generate uniform conductive network structures, leading to the production of carbon-silicon (C@Si) materials characterized by enhanced electronic conductivity, heightened chemical stability and strong adhesion to the current collector.

As an example, Wang et al. [86] investigated the impact on electrochemical performance by adjusting various ratios of carbon and silicon in LIBs anodes. The Si/C ratios were determined based on the thickness of each Silicon and Carbon layer, synthesized through a magnetron sputtering method. The optimal ratio for the thickness of film layers was identified as 15 nm for Silicon and 5 nm for Carbon. This configuration yielded charge-specific of 2560  $\text{mAhg}^{-1}$ , initial discharge capacities of 2640  $\text{mAhg}^{-1}$  and an "initial coulombic efficiency (ICE)" of 97 %. Moreover, the produced anodes exhibited a capacity retention of 87 % after 200 cycles. Similarly, He et al. [87] developed a porous carbon framework (PCF) for LIB anode via a straightforward technique using grape stems. At first, the authors produced carbon materials and then mixed with "tetraethyl orthosilicate (TEOS)" as the source of silicon. Finally, the developed composite underwent reduction through a magnesium heat treatment technique (see Fig. 8 for more details). As in Fig. 8, the composite of PCF/Si demonstrated a commendable discharge capacity of 1006  $\text{mAhg}^{-1}$  and cycling stability of 891  $\text{mAhg}^{-1}$  after 400 cycles. Overall, addressing these challenges requires a combination of experimental optimization, innovative synthesis techniques and materials characterization.

## 7. Comparing the electrochemical performance of Si/C composite anodes derived from agro-waste and composite anodes made from conventional chemical precursors

As illustrated in Table 2, the Si/C composite derived from agro-waste exhibits comparable or even superior capacity and initial capacity compared to those made from conventional chemical precursors. Si/C composites made from agro-waste may have distinctive morphologies and structures as a result of the particular processing techniques employed. Superior electrochemical performance can result from these architectures' increased lithium ion diffusion paths, improved electrode-electrolyte interactions, and greater capacity to accommodate volume variations during cycling. Also, the electrochemical performance of the composite anode may be further improved by the synergistic effects of combining silicon obtained from agricultural waste with carbonaceous materials. While silicon

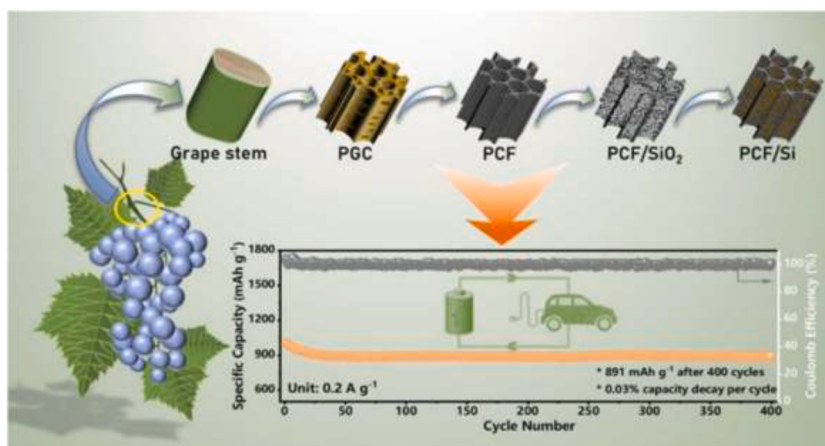


Fig. 8. Preparation of PCF/Si anode and the electrochemical performance from He et al. [87].

adds to high specific capacity, the carbon matrix can offer mechanical support to reduce silicon expansion or shrinkage during the cycle. This comparison helps to determine the suitability of agro-waste-derived materials for practical applications.

## 8. Different carbon materials used for producing Si/C composites anodes

Si/C composite anodes require carbon components for structural integrity, electrical conductivity, and buffer volume change that occurs during the lithiation and delithiation of silicon. Several studies have conducted research using different carbon materials and the commonly used carbon materials include activated carbon, graphene, carbon nanotubes and many others. Activated carbon also referred to as porous carbon materials is characterized by disorder and possessing small pores along with large surface areas. Typically, activated carbon is produced through the thermal decomposition and partial oxidation (known as activation) of various organic sources, whether natural or synthetic. Widely regarded as a traditional and prevalent type of porous material, activated carbon holds a prominent status in the field [92]. This material serves several purposes inside the electrode structure. First of all, because of its highly porous nature, it has a large surface area that can accommodate the volume changes brought on by the lithiation and delithiation processes of silicon. Moreover, activated carbon serves as a matrix that conducts electricity, promoting electron movement across the electrode. The inclusion of activated carbon in Si/C composite anodes in LIBs improved overall performance and cycle stability due to the combination of structural support and electrical conductivity. Sekar et al. [6] developed a Si/C composite anode using “activated carbon-decorated spherical silicon nanocrystal” obtained from rice husks. The authors reported that the inclusion of the activated carbon with good electrical conductivity and high porosity plays an important role in the composite and it results in “high reversible specific capacity (429 mAh/g after 100 cycles), high discharge capacity (716 mAh/g) and high coulombic efficiency (97.5 %)”.

Another carbon material used is graphene, a single layer with exceptional mechanical and electrical conductivity, organised in a two-dimensional honeycomb lattice. Adding graphene to Si/C composites can enhance the electrode's structural stability and electrical conductivity. Yi et al. [93] produced a “dual conductive network-enabled graphene/Si–C composite anode” and the results show that the addition of the graphene gave a high coulombic efficiency (99.51 %) and high areal capacity (3.2 mAh/cm<sup>2</sup>). It shows that graphene might have enhanced the electron transport within the electrode leading to improved capability and cycling stability. Also, the graphene acts as a protective layer for silicon particles minimizing the deterioration of them over repeated cycles of charge and discharge.

Table 2

Comparison of the performance metrics from Si/C derived from agricultural waste and composite anode from conventional chemical precursor.

| Si/C derived from agricultural waste                 |                                                                       | Performance metrics                                |                                         |
|------------------------------------------------------|-----------------------------------------------------------------------|----------------------------------------------------|-----------------------------------------|
| Author(s)                                            | Source                                                                | Initial discharge capacity (mA h g <sup>-1</sup> ) | Capacity retention                      |
| Liu et al. [26]                                      | Waste coffee grounds and Rice husks                                   |                                                    | 1125 mAhg <sup>-1</sup> , 100 cycles    |
| Chen et al. [28]                                     | Sugarcane leaves                                                      | 138.6                                              | 1562.8 mAhg <sup>-1</sup> , 400 cycles  |
| Wang et al. [40]                                     | Reed leaves                                                           | 650                                                | 1548 mAhg <sup>-1</sup> , 200 cycles    |
| Sekar et al. [6]                                     | Rice husk                                                             | 716                                                | 429 mAhg <sup>-1</sup> , 100 cycles     |
| Composite anode from conventional chemical precursor |                                                                       |                                                    |                                         |
| Zheng et al. [88]                                    | Nanosized Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> /C          | 176.2                                              | 163.7 mA h g <sup>-1</sup> , 100 cycles |
| Jhan and Duh [89]                                    | Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> /MWCNT                | 166.0                                              | 161.0 mA h g <sup>-1</sup> , 100 cycles |
| Yi et al. [90]                                       | Li <sub>4</sub> Ti <sub>4.85</sub> Mo <sub>0.15</sub> O <sub>12</sub> | 278.3                                              | 220.7 mA h g <sup>-1</sup> , 100 cycles |
| Li et al. [91]                                       | Mesoporous LTO/Au spheres                                             | 154.1                                              | 149.2 mA h g <sup>-1</sup> , 100 cycles |

Carbon nanotubes (CNTs) are another carbon material used due to their high electrical conductivity and mechanical strength, making them attractive materials in produced Si/C composite anode. CNTs offer effective routes for electron transport when added to Si/C composite anodes, enhancing the electrode's total conductivity. Furthermore, CNTs can improve the rate performance and cycle stability of the LIB by reducing the volume expansion of silicon during lithiation. Akbulut et al. [94] developed "a novel free-standing Si/C/Mutli wall carbon nanotubes for high energy battery applications". The developed composite has a mesoporous structure and the size of the pore lies between 200 nm and 2  $\mu$ m and the carbon nanotubes offer the composite a large surface area for volumetric changes. The samples gave a stable capacity (1290 mAh/g) after 200 cycles. Overall, the creation of high-performance LIBs with improved energy storage capacity and extended cycle life appears to be promising when CNTs are included in Si/C composite anodes.

## 9. Conclusion and prospects

The exploration of agro-waste for the production of electrode materials in LIBs is driven by the aspiration to create environmentally friendly materials and sustainable energy storage devices. Agro-waste-derived materials have garnered significant interest and hold substantial potential for the development of anodes in LIBs. They contribute positively to fostering a circular and sustainable economy. However, before reaching full maturity for use in industrial applications, substantial obstacles need to be addressed. Presented below are the outcomes, challenges, and perspectives.

1. Significant challenges are linked to the choice of the kind of agro-waste and the identification of appropriate synthesis techniques for developing or optimizing high-performance anode materials. The properties of the synthesized carbon material are notably affected by the selection of precursor materials; however, there is a need to establish specific criteria. In future research, a more comprehensive understanding of the composition of agro-waste precursors is generally essential.
2. The significant difficulty of changing the volume of Si anodes may be overcome by adding carbon through the formulation of bio-carbon materials with precisely engineered porosity. This porosity mitigates the problem by providing the space required to allow silicon's volume growth.
3. The key difficulties encountered with Si/C materials primarily revolve around the expansion in volume and the subsequent fragmentation of the ultimate anode. Addressing these challenges involves (I) selecting an appropriate agro-waste precursor and ensuring efficient conversion of waste into Si/C, (II) achieving uniform distribution of carbon and silicon in the optimal ratio, and (III) establishing a more stable bond between carbon and silicon materials.
4. To determine the true applicability of such technology in comparison to existing techniques, a Life Cycle Assessment (LCA) and a realistic economic study of the availability of agro-waste sources are needed.
5. Surface modification or coating techniques can be used to improve the reactive surface area of the compounds. Additionally, establishing an artificial solid electrolyte interface (SEI) on silicon before cycling can impede its reaction with the electrolyte, thereby improving the initial Coulombic efficiency.

## CRediT authorship contribution statement

**Adetomilola Victoria Fafure:** Writing – review & editing, Writing – original draft, Validation, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Daniel Barasa Bem:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software. **Stanley Wambugu Kahuthu:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration. **Adeolu Adesoji Adediran:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation. **Michael Oluwatosin Bodunrin:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision. **Abosede Adefunke Fabuyide:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision. **Christianah Ajanaku:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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