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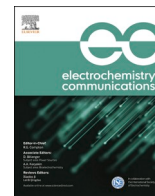
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Biomass-derived carbon–silicon composites (C@Si) as anodes for lithium-ion and sodium-ion batteries: A promising strategy towards long-term cycling stability: A mini review

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ABSTRACT

The global need for high energy density and performing rechargeable batteries has led to the development of high-capacity silicon-based anode materials to meet the energy demands imposed to electrify plug-in vehicles to curtail carbon emissions by 2035. Unfortunately, the high theoretical capacity (4200 mA h g⁻¹) of silicon by (de-)alloy mechanism is limited by its severe volume changes ($\Delta V \sim 200\% - 400\%$) during cycling for lithium-ion batteries (LIBs), while for sodium-ion batteries (NIBs) remain uncertain, and hence, compositing with carbons (C@Si) represent a promising strategy to enable the aforementioned practical application. The present review outlines the recent progress of biomass-derived Si-carbon composite (C@Si) anodes for LIBs and NIBs. In this perspective, we present different types of biomass precursors, silicon sources, and compositing strategies, and how these impact on the C@Si physicochemical properties and their electrochemical performance are discussed.

1. Introduction

Lithium-ion batteries (LIBs) have attained interesting progress in modern society due to the huge consumption of mobile electronic devices and plug-in electric vehicles (EVs). Despite LIBs spectacular commercial adaptation and being the frontrunner among all rechargeable batteries, the future of LIBs is still uncertain due to the shortage of lithium as well as other raw materials (nickel and cobalt) [1–6]. These issues have led to an unstoppable search for new, greener, and cheaper battery systems such as sodium-ion battery (NIB), which the first commercial prototype was announced by CATL battery manufacturer in 2021 [7]. However, China Three Gorges Corporation (reported in arena.v.com) first commercialized NIBs, in 2022, with an energy density of 145 Wh/kg that can endure 4,500 cycles. Graphite (Gr) is the commercial anode for LIBs and its theoretical specific capacity is limited to only 372 mA h g⁻¹, while for NIBs, its mechanism fails to intercalate

Na⁺, which undermines the requirements for high energy density devices [8]. The battery energy density (W h kg⁻¹) is intrinsically linked to the cell voltage (V) times the capacity of the electrode materials (mA h g⁻¹). However, compared to the cathode materials, the anode is the critical component to increase the battery's specific capacity.[9–11] Currently, many strategies dedicated to anodes' fabrication targeting its use on LIBs and NIBs have been explored such as metal–organic frameworks [12], transition metal composites [13,14], conducting polymers [15], metal oxides/hydroxides [16], carbon materials [17–19] and carbon composites [20–23]. Among these, carbon composites appear to be a promising strategy to prepare high-performance anodes for LIBs and NIBs due to their a) easy preparation, b) sustainable approach, c) high specific surface area, d) tunable microstructure morphology, and e) flexibility of compositing with many types of high energy density elements like silicon (Si).

Si possesses an extremely high theoretical capacity of around 4200

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mA h g^{-1} , making it a suitable candidate to replace or supplement Gr anode materials [24], despite their low electrical conductivity and a severe volume expansion ($>200\%$) upon cycling. The latter cause the Si anode pulverization leading to loss of electrical contact resulting in rapid capacity fading during their charge/discharge process making it difficult to realize the full potential of silicon as a high energy anode material for LIBs and NIBs. The volume expansion provoked by alloying and de-alloying of Li^+ or Na^+ ions cause cracks for pure Si anodes due to an unsustainable mechanical stress. Two main failure mechanisms are highlighted (in Fig. 1a,b): a) Upon (de-)alloying with Li^+/Na^+ , the silicon undergoes huge volume change resulting in irreversible particle pulverization due to the induced stress; b) secondly, due to the rupture of thick irreversible solid-electrolyte-interface (SEI) layer along with partial or total disconnection of anode layer from current collector provoked by the interfacial stress that is huge in pure silicon anodes. These two main failures accelerate anode capacity fading and cell collapse. In addition, the serious volume changing contributes to the sluggish electrochemical kinetics [25]. The choice of liquid electrolyte can partially mitigate the silicon by the formation of stable SEI [26,27]. To overcome these two main failure mechanisms, compositing Si with carbons can serve as stress-relief buffers to alleviate the volume expansion and provide more stable contact with current collector as highlighted in Fig. 1c,d.

Therefore, C@Si based anodes are promising anode composites due to the relatively low cost, abundance of precursors, high energy density, and sustainable cycle life in electrochemical energy technologies. So far, several Si/C composites have been fabricated and employed in LIBs including by using carbon nanotubes [28], graphene [29], Gr [30], and biomass-derived carbons [17]. Among these materials, biomass derived carbon materials have been widely employed for compositing with silicon (C@Si) because of their good electronic conductivity, low-cost effectiveness, high relative abundance and ability to effectively mitigate the volume expansion of Si. In fact, biocarbon's are rich and easy to be functionalized at the surface which helps in making covalent bond and/or van der Waals forces of attraction by self-assembly with silicon atoms to make a C@Si composite/hybrids [31].

The growing academic interest in developing biomass side streams as carbon source for anodes fabrication is very latent due to the high number of published articles worldwide over the last decade [32–38]. This review addresses the recent progress of biomass derived Si/carbon composites/hybrids anodes for LIBs and NIBs summarizing different types of biomass precursors for Si and carbon, and compositing strategies and their impact on the C@Si physicochemical features and electrochemical performance are discussed. Finally, the crucial obstacles related to applying biomass-silicon based anodes in LIBs and NIBs are described, and potential future research directions are pointed out. Based on the literature considered in this review, we expect that this

work could further interest scientists worldwide who seek out novel, easy synthesis and sustainable C@Si anodes from different biomass sources, aiming to open new strategies for the development of sustainable next generation of high efficient batteries.

2. Biomass-carbon silica composites strategies preparation

Si and C are the most abundant elements on the earth's crust which are vital for synthesizing functional materials for electronic transistors, photovoltaic and for energy storage applications. Due to high affinity of silicon toward oxygen, it can be extracted in the form of oxide (SiO_2) or silicates (SiO_4). Therefore, the production of high purity ($>95\%$) Si involves high temperature in reducing conditions, and energy-expensive carbothermic reduction process resulting in solidified Si which in fact couldn't be used directly in battery application as the particle sizes should be in the nanometre range [39–42]. The latter preparation from silane and Si halides also involves tedious and high-cost procedures to produce nano-Si [39]. Therefore, it's urgent to develop low cost and commercially sustainable effective strategy to extract nanostructured Si for developing clean energy harvesting and storage devices.

The metallurgical grade Si that is produced by applying high temperature blast furnace with release of several tonnes of CO_2 is infinitesimal as compared to the quantity of Si cycled (via orthosilicic acid-silica-orthosilicic acid) through biomass [42–44]. Globally, it is estimated that plants intake 2.0 – 5.5 billion tonnes of Si/year [45–47], and typical examples of Si stores being, sugarcane, bamboo, rice husks etc [43,48,49]. The plant constructs an outer SiO_2 layer to protect itself from exterior invasion and possible ventilation to retain the moisture content between interior and exterior through its distinctive porous structures. After the declaration of Tesla Inc. to replace classical graphite with silicon anode in their upcoming EVs by 2020 the mass production of Si nano-architected materials became urgent. Unlike, the conventional high temperature blast furnace method, the production of biogenic nano-Si from biomass primarily involves 2 steps: (a) acid treatment to leach out metal impurities to obtain biogenic nano-silica followed by (b) metallothermic reduction using Mg or Al at moderate temperature to produce Si ($\text{SiO}_2 + 2\text{Mg} \rightarrow \text{Si} + 2\text{MgO}$) [50,51,52]. As of now, extensive morphological transformation of Si from pristine bulk ingots into nanoparticles, nanospheres, nanowires were obtained to mitigate its major drawbacks that includes: (a) its poor electronic conductivity ($1.67 \times 10^{-2} \text{ S cm}^{-1}$) and (b) huge induced stress and strain associated with volume changes and formation of thick SEI over Si surface resulting in (dis-)integration of Si during (de-)alloying process and hence, hampering nanostructured Si as sole active material in the long run.

Fig. 2 illustrates two different synthesis routes for C@Si preparation. Fig. 2a shows a synthesis process combining the following steps [42]:

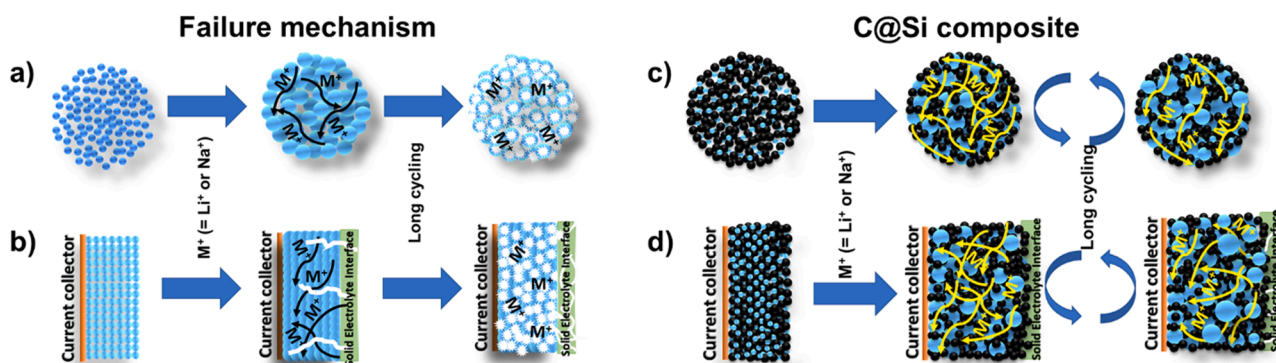


Fig. 1. Two important failure mechanism of Si electrode and positive effect of compositing Si with carbon materials (C@Si): a) pulverization of silicon particles; b) collapse of the entire sole silicon electrode; c) reduction of pulverization and increasing of cycling life in C@Si and d) possible healing mechanism in C@Si and a more stable contact with current collector.

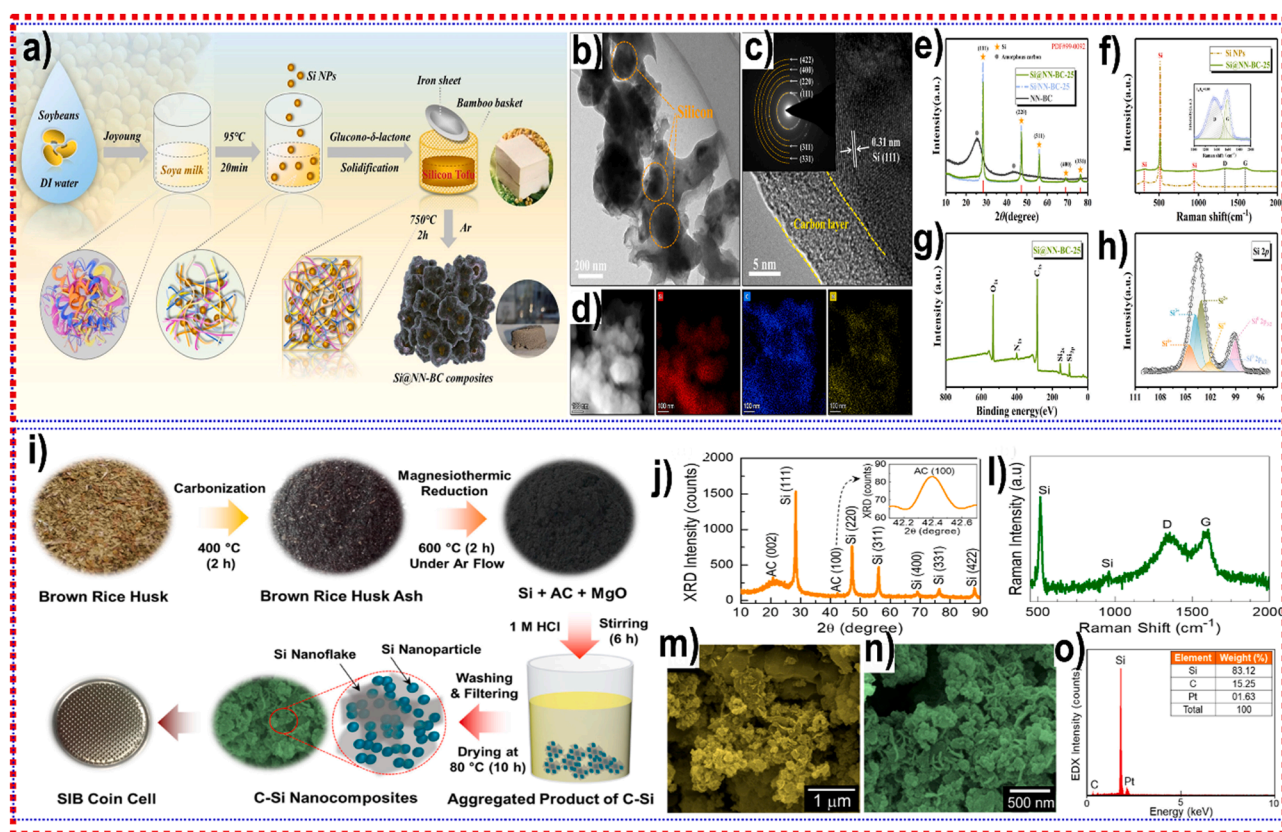


Fig. 2. A) illustration of c@si synthesis. b) tem image, c) hrtem image, d) stem image with the corresponding elemental mappings (si, c, and n) of c@si, e) xrd patterns of c@si samples, f) raman spectra of si c@si samples. inset: an enlarged view of the selected area, (g) survey xps spectra of c@si and (h) si 2p high-resolution spectrogram. Reproduced from with [73] permission from American Chemical Society. i) Illustration C@Si synthesis via magnesiothermic reduction, j) XRD patterns and (l) Raman spectrum of C@Si. Inset: of (a) displays the zoom-in view of the AC (1 0 0) peak, (m) Low-magnification FE-SEM image, (n) High-magnification FE-SEM image, and (o) EDX spectrum of the C@Si. The inset of (o) summarizes the compositional properties of the C@Si materials. Reproduced from with [67] permission from MDPI.

Biomass based on soybeans was mixed into a soybean milk, which is rich in protein and it serves also as nitrogen source. The mixture was heated at 95 °C for 20 min to precipitate the protein into silicon tofu gel and applying a freeze-drying process, a monolith was obtained. To obtain the final anode material, the monolith was at 750 °C for 2 h. The Fig. 2 b-h shows the physicochemical characterization, which proves the synthesis route proposed in Fig. 2a successfully created C@Si rich in silicon which later succeed in anode for LIBs application. Fig. 2i represents an easy synthesis of C@Si anodes through magnesiothermic reduction using rice husk precursor [43]. The physicochemical characterization (Fig. 2j-o) of the composites displayed aggregated morphology, where Si nanoparticles (around 9 nm) and the carbon structure were encapsulated and decorated with each other yielding anode materials with improved electrochemical performances for NIBs.

It is worth mentioning that the bio nano-Si exhibited enhanced physicochemical properties such as conductivity and specific surface area which help delivering a better cyclability only for few cycles compared to its bulk form [32,53,54]. This feature is mainly associated with the huge volume increase at the atomic scale (about 200 %) as it alloys with 4.4Li⁺ and reduced volume upon dealloying resulting in pulverization of nano-Si due to induced mechanical strains during cycling. Therefore, biogenic nano-Si is made of conductive carbon coating and/or composites/hybrids with high surface area porous carbonaceous materials like graphene, carbon nanotubes (CNTs) and mesoporous carbon, etc as an effective approach to serve the following advantages [32,53–55]: (a) enhance the electronic conductivity by providing shortest electrons transport from silicon electrode to the current collector; (b) increases the electrode–electrolyte interfacial

contact thereby stabilizing the SEI layer; (c) provide fastest lithium ions transport; (d) helps “anchoring” the biogenic nano-Si by covalent or van der Waals interaction thereby “buffering” volume changes during cycling. These nano-Si/C composites can show high theoretical capacity. However, the preparation of the composites is challenging and in general, a surface functionalization is thus necessary to enable self-assembly by van der Waals attraction forces. This strategy showed an excellent cycling performance upon constructing Si composites with graphene and CNTs [43]. In general, ex-situ synthesis methods have been used to prepare hybrid composites or carbon coating over biogenic nano-Si obtained by microwave-assisted magnesiothermic reduction and made composite with only few wt.% of pre-functionalized graphene and CNTs [42]. The ex-situ carbon coated were obtained using hydrothermal-assisted using precursors such as glucose and polymer carbon source like polyacrylonitrile, polydopamine etc by electrospray technique followed by carbonization at 600–800 °C to obtain C@Si composites/ hybrids [32,53].

However, the scale up process of these porous conductive high surface area carbonaceous materials is challenging and involves high production costs. The disadvantage related to the carbon coating process over nano-Si involves its irregularity and difficulty to optimize the coating thickness concerning their electrochemical performances. Therefore, opting for biomass as carbon source is an interesting approach to composite biogenic nano-Si due to following advantages: (a) ease of large-scale production from sustainable biomass resources [56]; (b) bio-carbons could be enriched with different physicochemical properties (high specific surface area, micro/meso porosity) with

tunable surface functional groups [57]; (c) in-situ formation of Si/C composites by leaching out other metal impurities from biomass sources [58]. Some processes about synthesized bio-based Si/C composites using abundant low-cost rice-husk biomass resources are reported in the literature: the composite contained between 14 and 15 wt% of biogenic nano-Si. Majeed et al [32] reported an initial discharge/charge capacities of 1309 and 841, respectively at 200 mA g⁻¹ with a retaining capacity of 781 mA h g⁻¹ after 300 cycles while Yu et al proposed a composite with an initial Coulombic efficiency (ICE) of 49.2% and 535.3 mA h g⁻¹ capacity after 200 cycles. Recently, Zhao et al [59], reported a novel molten-salt electrolysis of SiO₂ to produce nano-Si where Mg₂Si alloy is served as anode and paired with a C-SiO₂ cathode in molten NaCl-KCl-MgCl₂. During the electrolytic step, anode releases two Mg²⁺ ions into the electrolyte resulting in nanostructured Si (with a surface area of 47.3 m² g⁻¹) while the C-SiO₂ cathode is reduced to form a new Si-C composite (with 96.3 m² g⁻¹) without generating any undesirable products like SiC. Upon testing their electrochemical performances against Li, nano-Si exhibited an initial discharge capacity of 3954 mAh g⁻¹ with 82.3% ICE and a discharge capacity of 1490 mA h g⁻¹ at 2 A g⁻¹ after 300 cycles while during charge, Si-C composite delivered 1603.2 mA h g⁻¹ initial discharge capacity with only 55.2% ICE and a stable 780 mA h g⁻¹ capacity retention for 200 cycles. The low capacity of these Si/C composites could be attributed to the low Si content but benefitted with high-capacity retention from high carbon content. Therefore, an optimum Si and carbon loading in a Si/C composite needs to be balanced to have a high reversible specific capacity and stable long cycle-life.

3. Main challenges to prepare biomass-carbon and silicon composites for high-performance LIBs anodes

A simple blend of graphite with silicon is challenging because of the issues already mentioned above related to the volume changes of Si. However, due to its extremely high specific capacity, Si has a huge influence on C@Si anodes capacities, and finding a right/suitable method for compositing Si/C is still unclear. Even in small quantities, Si can provoke important capacity changes in the C@Si anodes. It's known that the C@Si anode cycle stability can be improved if the carbon content is increased, while it reduces the specific capacity.

In order to overcome the formation of a very unstable SEI layer [60], after the loss of contact due to volume expansion, some approaches can be taken in account. For instance, instead of graphite, biomass-based carbons (hard and soft carbons) that are rich in functionalities and heteroatoms (with more surface activity), may improve the electrochemical performances. In addition, because of the high surface activity biomass-based carbons are easily modified through heteroatoms and metal doping, and these strategies can help to increase the C@Si physicochemical and electrochemical stabilities [32]. Another option is to combine different forms of carbon (made from different types of biomass precursors and synthesis methods) with Si to create uniform conductive network structures and to fabricate C@Si materials with improved electronic conductivity, good adhesion to current collector, and high chemical stability.

For instance, Wang et al., [61] studied the effect on electrochemical performances by tuning different Si and C ratios (through Si/C multi-layer films) as LIBs anodes. The ratio of Si and C were calculated based on the thickness of each Si and C layers that were synthesized by a magnetron sputtering method and deposited on copper foil. The best ratio of Si/C film layer thickness was found to be Si (15 nm)/C (5 nm), which delivered an initial discharge and charge specific capacity of 2640 and 2560 mA h g⁻¹ respectively (ICE of 97%) and exhibited capacity retention of 87% after 200 cycles. He et al., [62] proposed three electrodes based on embedding silicon in biomass-derived porous carbon frameworks (PCF) for LIBs: the authors firstly prepared carbon materials and were subsequently blended them with silicon by using tetraethyl orthosilicate (TEOS) as Si source. Finally, the composite was reduced by

using magnesium thermal treatment method (See Fig. 3a for more details). The samples were labelled based on the amount of silicon in its structure as follows: H-PCF/Si (39% of Si), PCF/Si (56% of Si), and L-PCF/Si (74% of Si). The authors reported that the textural/morphological properties of the biocarbon, with big pores, and abundant oxygen functionalities, provided the suitable conditions to attach the Si on its structure, which led to sufficient space to accommodate volumetric expansion. Additionally, the as-synthesized porous structure was able to facilitate the electrolyte penetration and electron transfer.

Among the three evaluated C@Si anode samples, PCF/Si composite exhibited the best performances (See Fig. 3b), which displays the cycling performances, after 200 cycles, PCF/Si displayed a highest specific capacity of 642 mA h g⁻¹ at 1 A g⁻¹. Moreover, PCF/Si also exhibited the highest discharge capacity equal to 1006 mA h g⁻¹ at 0.2 A g⁻¹, with a robust cycling stability (891 mA h g⁻¹ at the end of 400 cycles). The differences on specific capacity can be attributed to the presence of different Si amounts. SEM images show the anodes before and after cycling (See Fig. 3c-h). After cycling, deep cracks were observed on the L-PCF/Si anode surface (Fig. 3h), which were attributed to the huge mechanical strain, due to the bigger volume expansion, provoked by the alloying of Si particles with Li⁺, and since the amount of Si in this anode is the highest, strongest if the collapse of the anode. This claim can be strengthened by observing the other anodes (h-PCF/Si and PCF/Si that observed smaller cracking phenomenon that may be improved by increasing the amount of C (less Si) in composites structure, which helped the anodes to better sustain stable structures by accommodating the volume changes.

4. Challenges of compositing biomass-carbon and silicon anodes for high-performance NIBs

The performance of NIBs relies to a good extent on the anode side, whose characteristics have strong influence on the charge/discharge mechanism.[63] Moreover, unlike in LIBs, the graphite is unsuccessful to form graphitic-intercalating-compound (NaC₆) but rather forms a thermodynamically, unstable NaC₆₄ compound upon Na-plating [64-66] which hinders the battery performance. Sankar Sekar et al [67] recently reported that biomass carbon-silicon (C-Si) nanocomposites via facile method using brown rice husk ashes as seen in Fig. 4: this nanocomposite delivered 378 mA h g⁻¹ (100 mA g⁻¹) of discharge capacity and a high reversible capacity of 122 mA h g⁻¹ (0.2 A g⁻¹) with a 98% CE even after 100 cycles. Based on this concept, the Si nanoparticles can be encapsulated with ultrathin C nanoflakes with high conductivity providing the intercalation/de-intercalation of sodium ions for C-Si nanocomposites for NIBs. The (de-)sodiation of silicon has been less investigated compared to (de-)lithiation. The sodiation in crystalline Si is very low due to the poor and low kinetics [68], while on amorphous Si is very possible. Na-Si phase diagram shows that the major sodiated phase is at composition 1:1, leading to a theoretical capacity of 954 mA h g⁻¹. He Gong et al [69] reported the pre-treatment of the acidic system helps to ensure the two-dimensional (2D) carbon sheet is embedded with Si via a high-temperature carbonization method. The 2D Si-C anode delivers at a specific capacity of 180 mA h g⁻¹ (0.2 A g⁻¹) with a retention rate of 94.6% for 1000 cycles. To tackle the present issues, promising strategies to fabricate C@Si materials are needed. Utilizing the biomass-derived carbons into Si/C composites will open a gateway for the development of NIBs applications as well as low-cost and eco-friendly preparation methods. Very few progresses were made in biomass derived Si/C anodes for NIBs applications and more efforts will be necessary in the future. Table 1 represents for the recent development of C@Si anode materials for LIBs and NIBs applications.

5. Technical and environmental challenges involving the selection of biomass as the precursor for C@Si preparation

In this review, we have shown that biomass-derived materials have

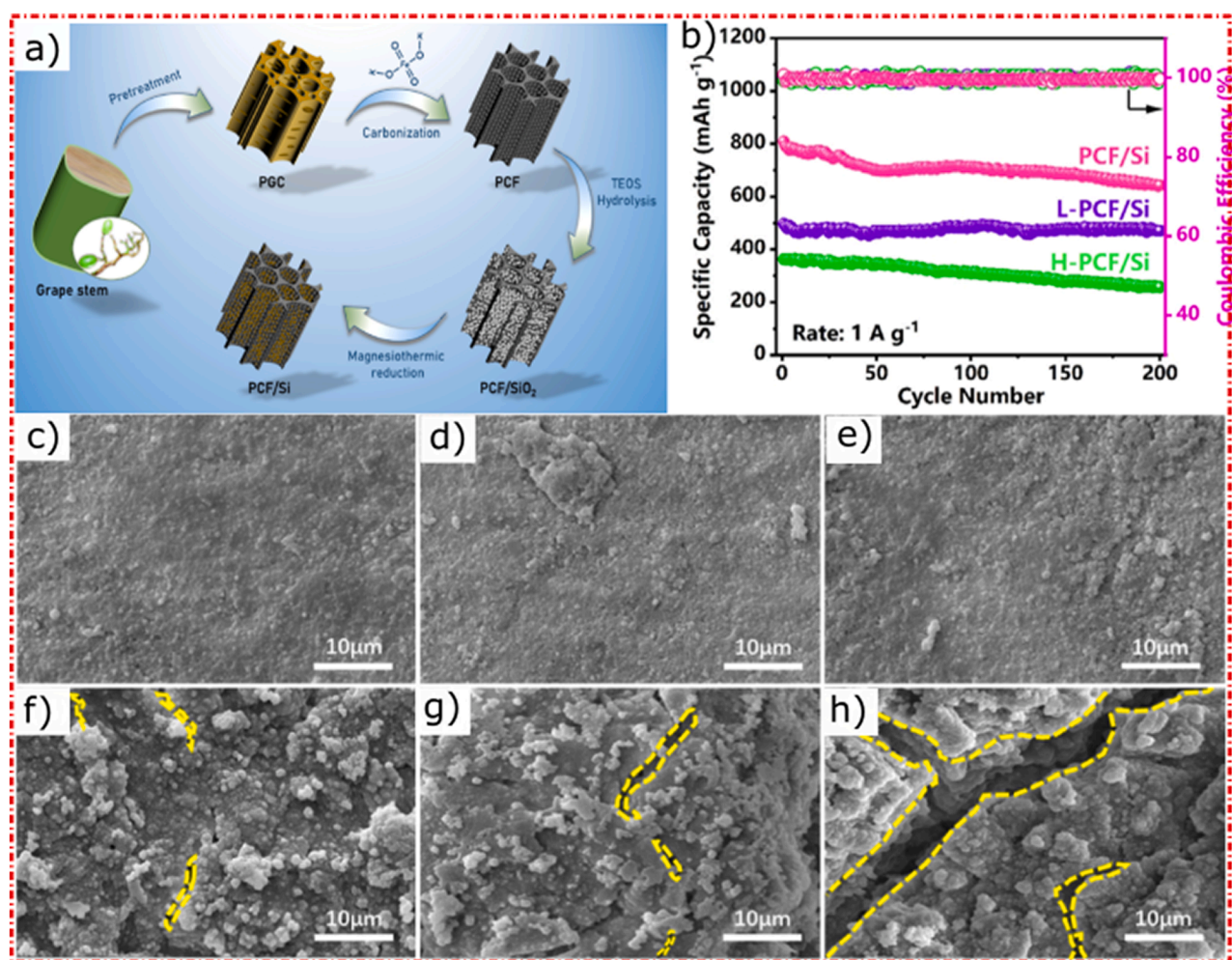


Fig. 3. a) Preparation method of C@Si; b) cycle performances; (c,d,e) scanning-electron-microscopy (SEM) images before cycling and after cycling (f,g,h). Reproduced from [62] with permission from Elsevier.

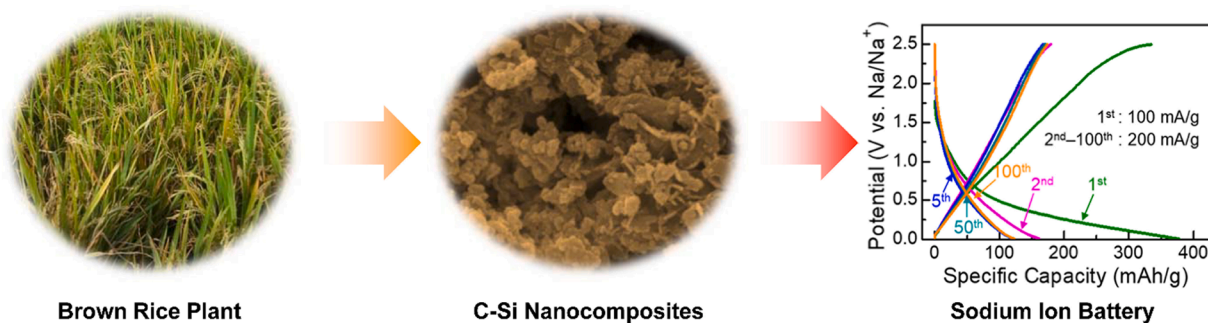


Fig. 4. An overview of the biomass brown rice husk to produce the C-Si nanocomposite anode materials for NIBs. The C-Si anodes with different current densities of 0.1 – 0.2 A/g. Reproduced from with [67] permission from MDPI.

attracted important attention due to their potential as the main precursor for developing anode materials for LIBs and NIBs as a beneficial source in promoting sustainability and circular economy. However, we must understand that the use and selection of biomass resources also face several issues related to their type and composition that varies from locally where they are generated. Moreover, the amount, type, and composition of biomass resources are also largely influenced by environmental, economic, policy, and social conditions in which are generated since all these aspects vary from country to country and within the countries.

For instance, feedstock unavailability regarding inefficient resource management can be a factor hindering the expansion of the biomass industry. Regional and seasonal availability of biomass results in variation in the biomass supply and possible impact on the prices and storage approaches. Pressure on shipping/transportation of the biomass resources as a result of their low density and high biomass moisture, becomes energetically unfavorable and costly with increasing distance. Issues related to feedstock acquisition cost should also be pointed out as a consequence that biomass resources are scattered and to reduce the cost of transportation, biomass projects are eager to occupy land close to

Table 1

Comparative electrochemical performance of biomass-based Si-C anodes for LIBs and NIBs. Ethylene Carbonate (EC), diethyl carbonate (DEC), fluoroethylene carbonate (FEC), dimethyl carbonate (DMC), vinylene carbonate (VC), N-methyl-2-pyrrolidone (NMP), poly (vinylidene fluoride) (PVDF).

Biomass source & Si source	Synthesis method	Anode composition	Electrolytes	Initial Discharge capacity /current density	Capacity retention	Ref.
Lithium-ion batteries (LIBs)						
Rice husks & Self conversion to Si	Thermal treatment and magnesiothermic reduction	c-Si RH + Super P + poly (acrylic) acid (60:20:20 wt%) NMP as a solvent	LiPF ₆ of EC and DEC 1:1, vol/vol) with 5 wt% FEC	1,554 mA h g ⁻¹	100%, 200 cycles	[49]
rice-husk (RH) biomass & Self conversion to Si/C	Heat treatment	Active materials + PVDF + Super P (80:10:10) NMP as a solvent	1.0 M LiPF ₆ in EC, DMC and DEC (1:1:1)	372.5 mA h g ⁻¹	100%, 80 cycles	[74]
Biomass lignin & self-assembly with Si nanoparticles	bath sonication	SINPs@ Lignin	1 M LiPF ₆ in EC/DEC/VC (4:3:3 v/v/v)	2798 mA h g ⁻¹	300 mA g ⁻¹ , 100 cycles	[75]
Reed leaves & Si/C hybrids fabricated by using CO ₂ (carbon source)	magnesiothermic reduction	Active Materials + Super P + sodium carboxymethyl cellulose + styrene butadiene rubber (60:20:10:10 wt%) deionized water as a solvent.	1 M LiPF ₆ in DMC/EC (1:1/v:v) + 10 vol% FEC	1548 mA h g ⁻¹ at 100 mA g ⁻¹	650 mA h g ⁻¹ , 200 cycles	[60]
rice husk (RH) & Calcination for self conversion to Si/C	Annealing	Si/C + acetylene black, + sodium alginate (SA) (70:15:15)	1 M LiPF ₆ in 1:1 (v/v) (EC/DMC) + 5% FEC	1368 to 398 mAh/g (100 to 3000 mA g ⁻¹)	500 mA g ⁻¹ , 300 cycles	[32]
Barley straw & Production of Si/C precursor from the acidic treatment	Heat treatment	Active material + sodium-alginate binder + ECP600 conductive Agent (70:20:10)	1 M LiPF ₆ dissolved in 1:1 EC:DMC	1180 mA h g ⁻¹ at 0.1 A/g	-	[76]
Sodium-ion batteries (NIBs)						
brown rice husk & Self-sourced Si	Carbonization and Magnesiothermic reduction process	C@Si nanocomposites + carbon black + PVDF (80:10:10 wt%) NMP as a solvent.	1 M NaPF ₆ (1:1, EC/DMC)	378 mA h g ⁻¹ / (100 mA g ⁻¹)	122 mA h g ⁻¹ (200 mA g ⁻¹ , 100 cycles)	[67]
corn cob & Self-sourced Si	high-temperature carbonization	Super P: PVDF: NMP (7:2:1:19)	1 M NaPF ₆ (1:1, EC/DMC)	181 mA h g ⁻¹ / (100 mA g ⁻¹)	~170 mA h g ⁻¹ (100 mA g ⁻¹ , 1000 cycles)	[69]

the source, leading to centralization of biomass projects.

Difficulties in studying the variability of feedstock composition/properties that is often considered as a major drawback when biomass is employed as the main precursor for materials development/fabrication since the methodology employed in its fabrication is severely dependent

on the biomass chemical composition and this varies based on biomass resource location. For instance, the SiO₂ content of the biosources mainly depends on the geological origin of the plants/trees, and it is known that each continent and country have very different geological formations and therefore is very difficult to tackle this issue.

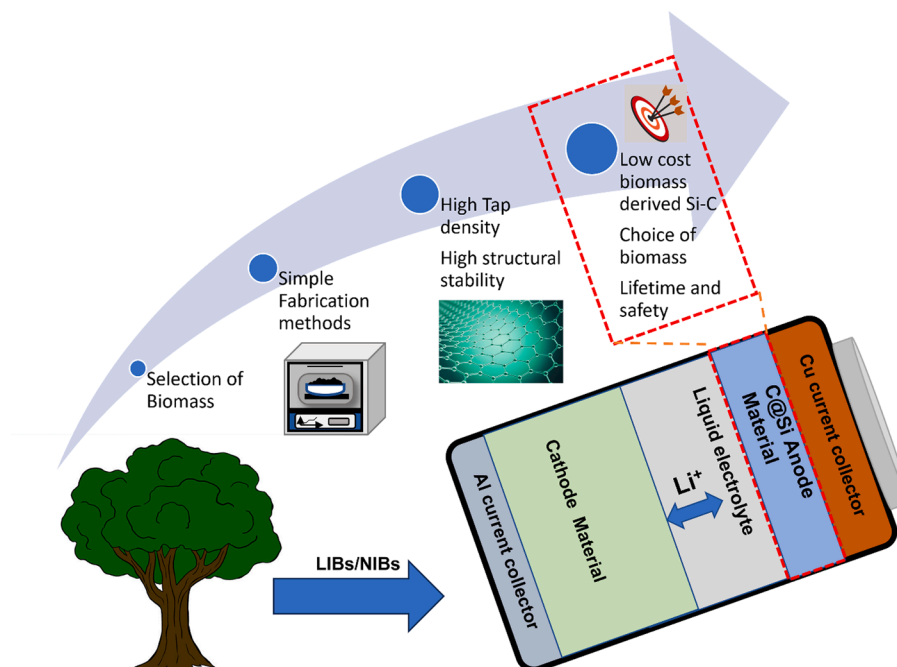


Fig. 5. Future directions of Biomass derived C@Si anodes for LIBs/NIBs.

Difficulties in measuring the biomass resources available by location as well as their prices (\$ per dry ton) are very difficult to be stated, depending on the location because many regions do not provide such data, especially cities in developing countries in South America, Asia, Africa etc. Also, the price changes from location to location based on how the crops and trees are harvested (equipment used and price of local energy) [70]. All these factors create huge difficulties in stating or predicting biomass generation and their prices. As the selection of precursor materials can significantly influence the properties of the synthesized carbon material, a selection criterion needs to be established. The difficulty of purifying the bio-based material to obtain high-quality bio-nanomaterial affordably should also be considered. A better knowledge of the composition of biomass precursors and how they affect the materials' final properties is required in future research (Fig. 5).

In addition, environmental aspects related to biomass resources uses must be pointed out, for instance, the presence of chlorine and heavy metals, etc. Washing and leaching can reduce chlorine concentration and other inorganic elements in agricultural biomass [8]. Xinliang Liu and Xiaotao T. Bi reported the reduction of chlorine content in biomass after washing by using water at higher temperatures or chemicals [71]. For instance, Cui et al. [72] reported an efficient method for reducing chlorine in biomass (banagrass), by initial mechanical dewatering followed by water washing and secondary mechanical dewatering. The chlorine content was reduced from 5350 ppm for the untreated feedstock to 2400 ppm after the initial mechanical dewatering. However, a further reduction to below 300 ppm after leaching with water and secondary mechanical dewatering was achieved. It is important to note that the techno-economic assessment of this method is a real issue because after leaching with water the biomass requires to be dried before C@Si composites preparation and that also requires a huge expenditure of energy use for drying the high moisture biomass after washing.

Insert Fig. 5.

Although biomass resources are potential precursors for the development of a wide range of materials including anodes for batteries, the aforementioned factors threaten the economic viability of biomass preprocessing and must be considered when choosing a feedstock for materials preparation. However, there is no doubt that despite all these issues biomass can still be considered a sustainable, green, and suitable source of materials for multiple applications including anodes for batteries.

6. Conclusions and outlook

The promising strategy to improve the electrochemical performance of C-Si composites, put this group of bio-based anode materials as highly potential candidates as LIBs and NIBs anodes. However, important issues need to be tackled before their full development. The following conclusions, challenges, and perspectives are outlined:

1. Important challenges associated with biomass resource selection and suitable for the development/optimization of corresponding cost-effective synthesis methods to achieve high-performance C@Si anode materials. The selection of precursor materials can significantly influence the properties of the synthesized carbon material, but a criterion needs to be established. Generally, a better knowledge of the composition of biomass precursors is required in future research.
2. The huge volume change issue of Si anode can be tackled/alleviated by adding carbon via compositing bio-carbon materials with well-developed porosity, which provides space to accommodate the volume expansion of Si.
3. Important challenges of C@Si materials are mainly associated with the volume expansion and fragmentation of the final anode. These challenges can be tackled by focusing on (i) The proper selection of biomass precursor and choice of suitable conversion efficiency of biomass into carbon and C@Si, (i) the uniform carbon mixing and the optimal ratio of Si:C; (iii) develop a more stable bonding between silicon and carbon materials.
4. Compared to LIBs, there is very little research in the field of C@Si anodes for NIBs, and the right principles/mechanism of energy storage are not fully understood and need further studies.
5. New approaches about the preparation of 3D porous structures of C@Si from various sources could be feasible, including the use of new biomass, mainly considering their sustainable and recyclable features.
6. Carbon-coating or surface modification are the few ways to control the high reactive surface area of nano compounds. Also, building artificial SEI on silicon before cycling could inhibit the reaction with the electrolyte and enhance the first Coulombic efficiency.
7. To conduct a relevant economic analysis of biomass sources availability and Life Cycle Assessment (LCA) to unveil the real suitability of such technology against current practice.

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.

Data availability

No data was used for the research described in the article.

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