Biomass Precursor

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Sodium-ion batteries (SIBs) serve as the most promising next-generation commercial batteries besides lithium-ion batteries (LIBs). Hard carbon (HC) from renewable biomass resources is the most commonly used anode material in SIBs. The biomass precursors have a highly oxygenated, crosslinked, and disordered structure, resulting in an irregular HC structure that cannot be graphitized and makes it difficult to build a standard model. A variety of biomass have been demonstrated to have the potential to become precursor materials for high-performance HC anodes. Compared to other HC precursors such as sugars and polymers, biomass precursors, with their wide range of sources, low cost, and environmental friendliness, are undoubtedly the most promising green HC precursor materials. Owing to the diversity of biomass, the selection of suitable and reliable biomass raw materials depending on geographical conditions is crucial to the manufacturing of HC. In some studies, biomass-derived HCs show promising electrochemical performance, but a safe supply of biomass is hard to achieve.

waste biomass | hard carbon | sodium ion batteries | sodium-ion storage

1. Origin Biomass

Origin biomass refers to raw biomass that is used directly in HC processing after harvesting. Seaweed [1], cotton [2], and trees [3] are all common origin biomass precursors. Origin biomass generally has a larger volume and a higher water content. These materials require more pre-treatment steps, such as grinding, drying, acid washing, and pyrolysis, to become suitable HC precursor materials [4]. In addition, these precursor materials have other well-established applications and are inherently valuable. This makes them inherently more expensive than other precursor materials. For example, timber prices in the market are at 430 USD/MBF [5], approximately equal to 260 USD/t. Therefore, the use of origin biomass as a precursor material for HC production would not only lead to a complex production process, but also increased production costs.

2. Biomass By-Product

Biomass by-products are residues from the harvesting and processing of biomass and are mainly classified as industrial, forestry, and agricultural biomass by-products. Industrial biomass by-products are mainly derived from food or material processing. For example, residual sugarcane bagasse from the sugar industry, which is currently at 145 USD/t on the market [6]. Purna et.al obtained an HC anode with a capacity of 290 mAh/g and an ICE of 70% using sugarcane bagasse as precursor [7]. Lignin, the by-product from the paper industry, is also a widely used HC precursor material [8][9][10].

Forestry by-products are mostly residues from the tree harvesting process, such as sawdust, roots, and bark. Compared to wood, these forestry by-products have a similar composition, but are more affordable. Sawdust, for example, is currently priced at 50–200 USD/t [11] and has greater potential as a HC precursor material.

Agricultural by-products are mainly residues from the transformation of crops into products. These include straw, stems, and leaves left over from the harvesting process, as well as shells and peels from processing.

Agricultural by-products are a diverse and abundant source of material for biomass waste. The type and quantity of agricultural waste may vary depending on geographical conditions. For instance, Turkey produces an average of 0.5 Mt of hazelnuts annually, generating a substantial amount of waste from hazelnut shells [12]. The United States, being the top producer of corn with 383.9 Mt in 2021/2022 [13], has an extensive amount of waste in the form of corn straw and cobs. Meanwhile, China generates nearly 700 Mt of straw waste annually [14]. In the view of this, the selection of HC precursors needs to be made based on geographical considerations. Most of the agriculture waste biomass by-product has been reported to have potential as a HC precursor material. A summary of promising HC products derived from various agricultural by-products, including the processing conditions and their electrochemical performances, are listed in **Table 1**. It can be seen that the electrochemical performance of HCs is quite good, with a capacity higher than 350 mAh/g, and an ICE higher than 70%.

Table 1. Comparison of agricultural by-products-derived HC anodes for SIB.

Precursor	Carbonization Temperature	Capacity mAh/g	ICE%	Capacity Retention	Ref.
Shaddock peel	1200 °C	430.5 (at 0.03 A/g)	67.7	97.5% after 200 cycles	[15]
Pinecone	1400 °C	370 (at 0.03 A/g)	85.4	90.3% after 120 cycles	[16]
Mangosteen shell	1500 °C	330 (at 0.02 A/g)	83	98% after 100 cycles	[17]
Lotus Stem	1400 °C	351 (at 0.02 A/g)	70	94% after 450 cycles	[18]
Waste cork	1600 °C	358 (at 0.03 A/g)	81	71% after 2000 cycles	[19]

3. Biochar

Biochar, a product from biomass pyrolysis [20], is one of the commercial products that is of interest as a precursor to produce HCs. Advantages of the use of biochar include safe raw material supply and high carbon efficiency. Both types of biomass mentioned above can be used in biorefineries and obtain the corresponding biochar products [21]. Compared to biomass and biomass by-products, biochar has a higher carbon content (>70%) after the pyrolysis process (300–900 °C) [20]. This means that there is a higher yield of HC in the carbonization process and fewer by-products (syngas, bio-oil), which reduces the waste treatment process and improves the economics. Moreover, the two-step heat treatment process also increases the graphitization of the HC, thus improving the performance of the HC anode [22]. However, biochar, as an energy product, is currently more expensive on the market, at around 200–500 USD/t [23]. Meanwhile, after carbonization, the HC structure still retains a certain degree of similarity to the precursor [24]. Rios used biochar from four biomasses with similar C (50%), H (6%), and O (41%) contents as HC precursor materials. HC anodes with different electrochemical properties were obtained under the same conditions, including: pine (323.8 mAh/g, 85%), ash wood (280 mAh/g, 79%), miscanthus (274.9 mAh/g, 80%), and wheat straw (224.4 mAh/g, 65%) [25]. This means that the raw material for biochar still has a significant impact on HC performance.

The sources of all three types of biomass are limited by geographical as well as industrial conditions. Therefore, the primary consideration in the selection of HC precursor materials is the local condition. Secondly, the HC structure will vary depending on the main components of the biomass precursor material (cellulose, lignin, or hemicellulose). Therefore, the relationship between biomass type and HC structure must be explained in order to establish the basis for precursor material selection. Alternately, the material can be structurally modified to improve the HC structure. Finally, the economics of the production process should factor into the selection of HC precursor materials. Based on the biochar yield of the pyrolysis process and the carbon content in the biochar for these three types of biomass material [26][27][28], to obtain 1t HC requires around 6 t of origin biomass (timber [29], water content is 20.9%; biocahr yield is 26%; carbon content in biochar is 81%; price around 1560 USD/t HC), 5.1 t of biomass by-product (sugarcane bagasse [30], water content is 6%; biocahr yield is 25.6%; carbon content in biochar is 81.5%; price around 739.3 USD/t HC), or 1t of biochar (carbon content above 99%; price around 500 USD/t HC (). Current prices for high purity HC (300 mAh/g, ICE > 80%) for SIBs and LIBs are around 1500 USD/t [31]. Controlling raw material costs and improving the performance of the final HC product are the keys to improving economics.

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