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Tracing the technology development and trends of hard carbon anode materials - A market and patent analysis

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ABSTRACT

As the demand for energy storage is expanding rapidly, concerns have been raised about critical raw materials used in lithium-ion batteries. Post-lithium batteries have the potential to provide a more sustainable option for energy storage by taking advantage of raw materials that are more abundant and unrestricted by supply chains. Sodium-ion batteries are one type that is currently the most widely discussed candidate in light of the approaching commercialization. The most promising anode material for commercial sodium-ion batteries that can be applied in large quantities in the near future is expected to be hard carbon (HC). However, neither the current state of HC's commercialization nor the trend in technology development has been investigated. This work uses an approach that combines literature investigation, expert surveys, and patent analysis to track the growth route of HC and identify potential obstacles. The analysis of 352 HC-related patents and existing production operations shows that the HC market is still in the early phase of market development. As of now, production capacities are limited due to a lack of market forces and uncertain demand. Uneven distribution of market and research activities, lack of information transparency of the upstream supply chain, and potential hype stemming from market immaturity are highlighted as potential challenges in the HC market. To accelerate the commercialization of HC, as a prerequisite for a successful introduction of sodium-ion batteries to the future market, more investment and efficient market conversion of R&D efforts are required. This article offers recommendations to promote the sustainable design and marketing plans of HC-based battery systems.

1. Introduction

The global ambition for a sustainable energy transition has led to an explosive growth in demand for batteries. While the fast-expanding market implies rapid advancements in battery technology, it also poses problems in terms of available resources [1], cost [2], supply safety [3], and environmental impacts [4]. In today's predominantly-used lithium-ion batteries (LIBs), raw materials such as cobalt, lithium (Li), and natural graphite are identified as critical resources by the US and EU [5,6]. The rapidly growing demand makes it even more challenging to maintain a stable supply chain of these scarce materials [7]. At present, material costs typically account for around half of the battery cost. The ratio of material costs will continue to increase as cell costs decrease, since the cost of scarce raw materials is expected to increase further [8]. New materials and technologies that avoid such critical raw materials are considered as a possible solution to these challenges. Moreover, since battery manufacturing occurs in different countries, it is difficult to identify social and environmental problems in upstream

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supply chains [9]. Also, it is hard to control the global supply chains through a uniform standard, which risks the sustainability of battery systems [10,11].

Post-lithium batteries consist of materials that are more abundant than lithium, such as sodium (Na) and potassium (K) [12]. Therefore, they can replace the Li-based energy storage systems with potentially lower costs [13], less environmental impact [14], and a more reliable supply [10]. Sodium-ion batteries (SIBs) are considered as one of the most promising post-lithium batteries [15]. Due to the shared electrochemical fundamentals with LIBs, SIBs can reach the market by leveraging R&D experience and existing production lines of LIBs [16]. Many research have investigated the commercialization trends of SIBs and reported recent SIB prototypes from start-ups such as FARADION, HiNa, and Natron [15,17–19]. In 2021, CATL also announced its first SIB prototype and the goal to establish an industrial supply chain by 2023 [17,20].

However, graphite, the common anode material in LIBs, cannot be used in SIBs due to the inefficient intercalation of sodium ions [30]. Therefore, a variety of material types have been discussed as potential anodes for SIBs, such as metal-based oxides/sulfides, alloys (phosphorus or tin), and Hard Carbon (HC) [21–23]. Among them, HC is considered as the most promising candidate for the first-generation SIBs given its outstanding specific energy and sufficient capacity at low redox potential [23]. Up to now, the successful use of HC as an anode material has been reported for many commercial SIB prototypes [15,17]. HC has potentially better environmental and cost performance, as it can be synthesized from a wide range of various precursors (Referenced earlier works provide more information on sustainability [24–26], manufacturability [27–29], and material properties [30,31]). Not only SIBs, HC has established itself as a potential alternative to graphite due to good stability and abundance of precursors for lithium- and potassium-ion batteries [32] and also plays a role for supercapacitor systems [33,34].

The first R&D activities of HC date back to the 1990s, when Dahn et al. investigated the structure of HC and insertion mechanisms of lithium- and sodium-ion [35,36]. In contrast to graphite and soft carbon, this non-graphitizable carbonaceous anode material has since been commonly referred to as HC. In recent years, much effort has been made to overcome the drawbacks of the HC anode and develop suitable cathode materials to achieve accelerated global commercialization. Possible routes for large-scale HC production and optimization strategies for commercialization of SIBs have also been continuously investigated in previous works [32,37–39]. However, research that provides holistic information on the global supply chain and the current market for HC is still lacking, and its technological development status and trends need to be identified. This work aims to fill this gap by applying an approach consisting of a literature review, expert surveys, and a patent analysis.

Patent analysis has been applied to statistically capture the historical development and technology trends in the field of batteries. Sick et al. [40] demonstrated the dominance of carbonaceous materials in the commercial LIB market by patent analysis. Patent analyses can also reveal the activities and intensity of patent filings in different countries and companies, closely related to an emerging technology's commercialization prospects. For instance, Ershadi et al. [41] identified China, the US, and South Korea as pioneers in the field of novel anode Fe_3O_4/graphene nanocomposites, possessing technological expertise in the form of patents. It is also possible to trace an emerging material or battery technology's technological life cycle (TLC) and forecast future trends using patent analysis. Based on related patenting efforts, Chayambuka et al. [42] concluded that SIB technology is entering a stage of rapid expansion. They found that anode-related patents make up a sizable ratio of the SIB patents (more than 50 % in some years) and most anode-related patents focus on HC anode, including efforts on its processing, precursors, and irreversible capacity. Baumann et al. [43] developed a patent-based approach to evaluate the innovation trend of LIB technology and identified their market maturity level in terms of TLC. This approach can also be applied to other battery systems or materials. Therefore, this work applies and adapts the method from Baumann et al. [43] to gain insights into the R&D development of HC technologies.

2. Approach

This study uses a framework incorporating qualitative market analysis and quantitative patent analysis, as presented in Fig. 1. The qualitative analysis enables identification of the technical state of the art, the potential challenges, and global market development based on multiple literature sources and the judgment of experts. The quantitative patent analysis shows activities, intensity, and interested companies in different regions and thus estimates the TLC and orientation of the HC technology. The two parts are interdependent and interact in this way: technology development and market trends obtained from the qualitative analysis are used to analyze the fluctuations of patent curves, while results extracted from the patent analysis can corroborate or refine the qualitative findings. Cross-valid and coupled results provide a picture of HC technology development and future direction. The implementation of each segment is described in the following subsections.

2.1. Qualitative market analysis

2.1.1. Literature review

The literature review focuses first on the current development of HC materials in terms of structure, synthesis, application, and manufactural appraisal. Next, essential information required to analyze the market's size and maturity level is extracted. Multiple documents and papers that reveal the technical knowledge and commercial information of HC materials are reviewed.

Peer-reviewed scientific articles [24,30,37,39,44–47] addressing the historical development and including interpretations of advances and applications of HC materials are first investigated. However, as commercial HC products have only been mentioned occasionally in previous scientific works, relevant commercial documents are studied, including product data sheets, manuals, patents, internet documents, and reports from institutions and companies. A part of information about the manufacturers and the properties of their HC products are obtained from these publicly available data. Documents of patents registered by the associated manufacturers are also considered to assess the actual technical specifications of the products. Correspondingly, a baseline for comparing different HC products is established by the literature review.

2.1.2. Expert survey

An expert survey has been conducted to obtain missing details and clarify the ambiguous parts in previous literature. The survey was conducted between January 05, 2021 and December 29, 2021. In total, 22 experts participated in the survey, including HC producers, suppliers, and technology developers from industry and academia. The questionnaires are offered in Supplementary information.

Producers and suppliers of commercial HC products were first contacted with an inquiry form (presented in S1.1), in order to gather information regarding manufacturing, e.g., throughput capacity, plant site, or sustainability, as well as details of products about electrochemical properties, delivery amounts, and prices. The upstream supply chain and precursors were also an important part of this inquiry. Five producer units and four supplier units from six different countries participated in this inquiry form.

As potential consumers, technology innovators in the field of batteries are knowledgeable about the actual quality and layout of different HC products. Discrepancies detected in the literature are discussed and ascertained with the help of these professionals. In this work, insights from academia and industry complement each other. Technology developers from six industrial and seven academic units took part in the survey either by responding to the questionnaire (presented in S1.2) or

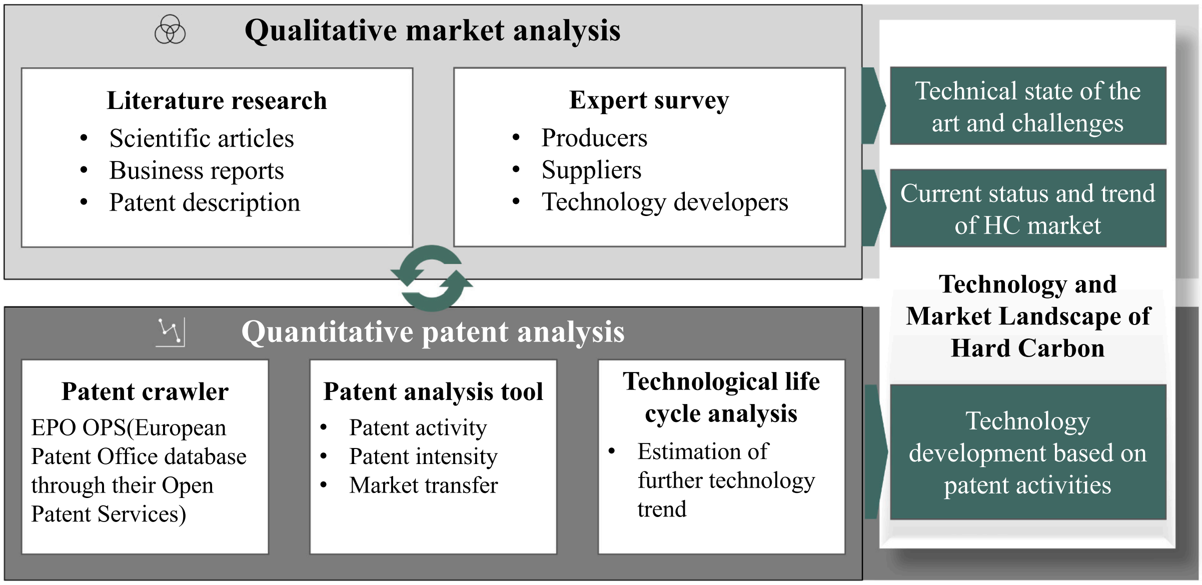

Fig. 1. The methodological framework of the study. Gray blocks indicate the two main types of research methods, white blocks indicate the specific approach and scope, and green blocks indicate the research objectives corresponding to the methods. As a result, critical insight into HC technology and market development can be obtained. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

agreeing to an interview.

Due to confidentiality issues, part of the specific data provided by the experts cannot be released. However, the results of the expert survey were developed into a report that discusses the technical state of the art and challenges associated with the prospective use of HC in batteries (presented in S2).

2.2. Quantitative patent analysis

2.2.1. Patent data collection

The patent analysis is conducted based on the framework developed by Baumann et al. [43]. In the first step, relevant patents are comprehensively chosen by a python-based crawler that applies the European Patent Office database through its Open Patent Services (EPO-OPS).

The patent analysis was carried out for patents from January 1995 until December 2021. Using "hard carbon" can be traced back to 1995 as a term to describe non-graphitizable materials as anode active materials, when Dahn et al. applied it for LIB [35]. Before that, some companies had established research on presumably identical materials but might have named the patent with other terms [48]. These are not represented in the analysis. The last patent retrieval was conducted on 07. January 2022. However, as a patent application can have up to 3 years of time lag after submission [49], the timeframe 1995–2019 is considered in this patent analysis to ensure robust data. The results include registered patents over time with all legal statuses (pending, active, discontinued, inactive, expired, unknown). As the legal status does not significantly impact the patent profile of HC, they are not distinguished in this study.

In the patent search, changing the settings of search terms such as keyword, concerned field, and concerned timeframe might reveal a different patent picture. By comparing search results based on full-text, abstract, and title, we found that the title-only search resulted in the most relevant results to the research goal, so only the title has finally been considered. To include all possible applications of HC, such as LIBs, SIBs, KIBs, supercapacitors, and fuel cells, as well as material fabrication and electrode process technology that are patented, the selection of IPC classification is broader in this study than in previous studies [40,41,50]. Explanations about the classification codes and a network map derived from the search result can be found in Supplementary information S3 and S4, respectively. The search terms were set as follows:

(ti = (hard carbon) or (non graphitizable carbon*) or (non graphitisable carbon*) or (hard graphitizable carbon*) or (hard graphitisable carbon*)) and ((ti = battery or ti = batteries or ti = anode* or ti = cathode* or ti = electrode* or ti = biomass* or ti = sodium or ti = lithium)) not (ti = (diamond) or (DLC)) and (cl = (H01M*) or (H01G*) or (B82Y*) or (C01B*) or (C04B*) or (C10B*) or (C25C*)) pd within '19950101 20211231'*

Synonyms of hard carbon, i.e., "non-graphitizable carbon" or "hard graphitizable carbon" are included [30]. Considering the inconsistency in transliteration, the words "graphitizable" and "graphitisable" are considered. It should be noted that in many cases of Chinese patents, the term "anode" is not translated correctly, and may be switched with "cathode"; therefore, the term "cathode" is also taken into account.

Moreover, the keyword "hard carbon" is not only applicable to the non-graphitizable carbonaceous anode material for battery devices. It is also used for diamond-like carbon film (DLC) materials, which pose a high hardness due to their dense structure [30]. DLC can also be used as coating or film for the electrode in the metal industry, so this diamond-like HC is confounding in the initial patent searches. To eliminate this impact, the term diamond and DLC is excluded. Accuracy of the corresponding patent data is checked manually.

2.2.2. Patent analysis

An Excel-based analysis tool [43] is employed, adapted, and further developed to analyze the patent activity for HC. The analysis of patent search results is divided into three parts: country-based, applicant/institution-based, and technology life-cycle analysis.

The first part is dedicated to comparing the patent activities according to the country of application. The preliminary patent analysis provides as an outcome a numerical order of R&D activities and historical development over the years. By separating and comparing the priority patents, family patents, and national patents of each country, it can identify the economic quality and international scope of the country-specific patents. To consider the differences in economic development and the degree of innovation between countries, and to compare the importance and focus of R&D in HC technologies in each country, a patent portfolio is presented based on three numerical indicators, calculated as follows [43]:

national technology share: represents the R&D strength of HC within a national scope:

$$NTS_{HC,t} = \frac{P_{HC,t}}{P_{a,t}}$$

$$P_{HC} : Patent\ number\ of\ HC\ related\ technology\ in\ concerned\ timeframe\ t$$

$$P_a : Total\ national\ patent\ number\ in\ concerned\ timeframe\ t \tag{1}$$

patent growth: indicates the growth rate of HC in the form of arithmetical mean of three-year interval (*t*) to evaluate the future growth potential:

$$Pg_{HC,t} = \frac{P_{HC,t}}{P_{HC,t-1}} \tag{2}$$

patent intensity: measures a country's level of R&D investment in HC based on its economic development by taking GDP (by purchasing power parity PPP) as the benchmark:

$$Pi_{HC,t} = \frac{P_{HC,t}}{GDP_{PPP,t}}$$

$$GDP_{PPP,t} : gross\ domestic\ product\ in\ accordance\ with\ purchasing\ power\ parity\ PPP\ in\ concerned\ timeframe\ t \tag{3}$$

The types of patent applicants are compared across countries, to learn the relationship between R&D behaviors and market development. Additionally, patenting across academia and industry is analyzed to identify where the original drivers of HC R&D come from. Furthermore, the patent number filed by concerned companies is traced back to recognizing the pioneers of HC R&D in the industry. These results are then correlated with the global HC manufacturing landscape identified in the previous qualitative market analysis to understand the R&D intensity of those identified market participants and their transferability from research to market. Finally, the annually published HC patents are fitted to the TLC curve, which allows display of the market maturity stage [49]. The current level of market development is estimated and taken as a criterion to measure further trends [27].

3. HC market analysis

3.1. Overview of market development

About 17 manufacturers in six countries are producing battery-level HC, as indicated in Fig. 2. Production capacity and supply are mainly located in East Asia, where China and Japan possess a clear dominance. European countries (Finland and Sweden) are also developing their own supply chains of SIB-materials, and there are two emerging manufacturers in the HC field.

It is possible to divide all these manufacturers into two groups regarding their backgrounds, as shown in Table 1. Some manufacturers are originally graphite anode or active carbon producers. Presumably, the R&D and manufacturing of HC can draw on the experience of graphite and other carbon forms. On the other hand, some companies whose primary business is HC precursors' production, such as phenolic resin or biomasses, can take advantage of the industrial chain to further process the precursors into HC. This allows them to exploit economies of scale, diversify their product portfolio, and improve profitability. Some battery manufacturers are also active in lab-scale HC investigation, and

Table 1
List of global manufacturers of HC anode materials classified by production capacity and country.

Countries	Pilot-scale production	Mass production	No information applicable
China	Shinzoom[a] Zichen[a] Bixidi[a] XFH[a] Yufeng Carbon[a]	Best graphite Shanshan[a] BTR[a,c]	
Japan		Kureha[b] Kuraray[c] Sumitomo Bakelite[b]	AT Electrode JFE Chem[a]
South Korea		Aekyung Petrochemical[b]	
Sri Lanka		HayCarb[a,c]	
Sweden			Biokol[a,c]
Finland	StoraEnso[b,c]		

[a] Manufacturers also produce graphite or active materials.
[b] Manufacturers also produce the precursors of HC.
[c] Manufacturers producing biomass-based HC.

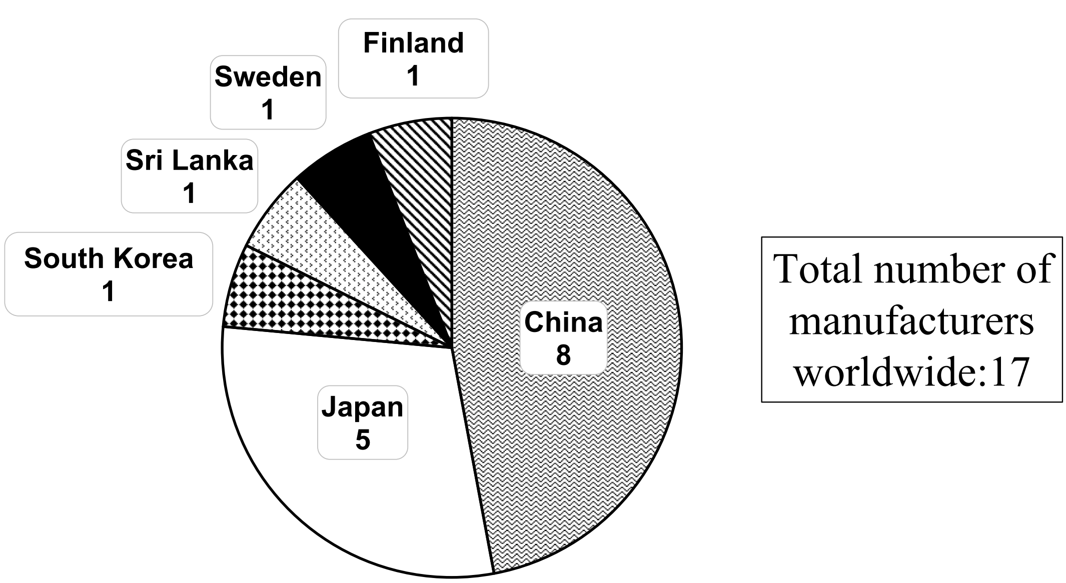

Fig. 2. Overview of global manufacturing of HC anode materials. The pie chart shows the countries where HC manufacturing takes place and the number of manufacturers in each country. (Only practical manufacturers are considered, which means suppliers, resellers, or distributors are not included in this figure.)

they hold proprietary technology or patents of HC materials. However, they are not included in this market landscape due to a lack of information.

Manufacturers from different regions can also be classified into two levels based on their manufacturing capacity: i) pilot-scale production, and ii) industrial-scale bulk production. The production scales are determined based on annual production volumes obtained through the producer questionnaires (S1.1), internet information, and commercial reports. Note that the definition and throughput to distinguish the pilot- and industrial-scale production is inconsistent, depending on the contexts and sources [51]. Here, the pilot-scale is defined with an annual capacity at kilogram level, i.e., under 1 ton per year, while mass production is set at the level of tons, i.e., over 1 ton per year.

The HC producers typically use the pilot-scale to optimize and test the product for client needs. Some pilot productions are carried out in laboratories with existing equipment and produce several kilograms of HC. In contrast, others, such as Stora Enso, invest considerable human and financial resources to build up a pilot line and aim to offer tens to hundreds of kilograms of HC per year. The latter is generally a starting point for optimizing mass production processes.

Currently, the industrial-scale plants for mass production are all located in Asia. The majority of Chinese HC is produced by graphite manufacturers that are entering emerging markets of SIBs. The manufacturing capacities of HC are usually not constant due to unpredictable demand. The Chinese start-up HiNa Battery claimed to achieve independent mass production of the SIB anode materials [52]. However, the company is excluded from the analysis as it is difficult to derive from available information [17,53] whether the anode material can be considered as HC or not.

According to the survey results, the current production capacity of Japanese firms is higher than Chinese firms. Japanese companies have gained extensive expertise in producing HC on an industrial scale for over 15 years. In the 1990s, Sony applied Kureha's Carbotron P™ as an anode material in the first generation of commercial LIBs, signaling the beginning of the industrialization of HC in small quantities [54]. In 2013, Kureha and the company Kuraray jointly commercialized a bio-version HC Kuranode™ and established a ton-level production and supply chain [55]. Sumitomo has also developed an industrial HC production line for high-power LIBs since 2012.

Large-scale plants can also be found in Korea and Sri Lanka. Aekyung Petrochemical has an annual output capacity of more than 100 tons. HayCarb provides tons of HC derived from coconut shells every year by leveraging the supply chain advantage located in a coconut origin country.

European producers have been emerging with a focus on biomass precursors. In Finland in 2021, Stora Enso established a trial line producing HC materials based on milled wood lignin, known as Lignode® [56]. Other units for mass production of HC on a scale of 80,000 to 100,000 tons/a are under development by Stora Enso [57]. As a member of NAIMA, a European project for building up commercial SIBs, the start-up Biokol is responsible for scaling up bio-based HC production by drawing on its research experience in activated carbon materials [58].

However, according to the expert survey, the production scale of HC manufacturers is not fully transparent in many cases. The mass production of HC is not in the same order of magnitude as that of graphite. Currently, bulk production for HC can reach roughly 500–1000 tons/a [55,57], while industrial plants of graphite typically have an (annual) production capacity of more than 10,000 tons/a [59]. For now, orders for HC are mainly from SIB manufacturers and developers, and demand for HC fluctuates as the SIB market is still in the initial development stage. Although some manufacturers have the ability to extend the scale quickly by adapting the production line, they currently would not exploit this option due to low commercial driving force and fluctuating demand.

3.2. Production potential and sustainability

The selection of precursors has a significant impact on electrochemical performance and sustainability [24,37]. The most common precursors utilized in current commercial HC manufacturing are wood lignin, coconut shell, coal, petroleum pitch, and phenolic resin. Their upstream supply chain and potential for producing HC are evaluated and shown in Fig. 3.

Producers select precursors based on their capabilities in the supply chain and technology accumulation. By-products of the petrochemical industry, such as coal tar pitch, are the traditional precursors of HC. The first generation of commercial HC produced in the 1990s was derived from petroleum coke [46]. These precursor materials are readily available through a well-developed supply chain. Later, it was found that biomass-derived HC also shows good performance in battery cells. The precursors based on biomass materials or wastes are usually presumed to be cheaper, more abundant, and more environmentally benign than precursors from the petroleum or coal industry [31,44,72]. As seen in Table 1, five concerned companies produce HC from biomasses. Kuraray and HayCarb use coconut shells [73,74], while Stora Enso begins with lignin separated from softwood [57]. BTR and Biokol use plant-based materials, whose composition and type are not provided in detail.

Fig. 3c shows the theoretical maximum production amount of potential HC from each considered precursor. It is calculated by the annual production of precursors and corresponding HC yields in fabrication, as follows:

$$P_{i,t} = M_i{}^* y_i$$

M_i : *annual production amount of raw material i worldwide*

Y_i : *yield amount of hard carbon produced from* 1 *kg raw material i*

Despite large potential amounts, petroleum- and coal-based precursors are highly demanded by other industries. Phenolic resin is currently the choice of most manufacturers, which is considered the least suitable precursor due to its lower production potential. In contrast, coconut shells are in most cases landfilled or incinerated as waste. Using them for HC preparation is a promising path to recycle biowaste. Note these are only theoretical calculations of the maximum production potential. If other key factors such as difficulties in collecting and processing the raw materials and maintaining the consistency during the production of HC are taken into consideration, the output potential might be affected.

In sustainability terms, the environmental impact of HC materials produced from different precursors has been investigated in previous studies. Coal-derived HC appears to have a better environmental performance in several impact categories, such as global warming potential, due to the high carbon yield and thus reduced raw material demand per mass unit of HC product [75]. Resin-based HC shows high impacts stemming from the upstream production chain, which is both energy- and emission-intensive [24]. In comparison, the supply chain of biomasses such as coconut shells and apple pomace is almost free of environmental burden, indicating that the biomasses have a high potential to become a sustainable source of HC [26]. However, a more in-depth environmental assessment is needed to estimate the environmental impact and consequential effect of producing HC on an industrial scale with different precursors.

The supply chain of HC is rather diverse, as HC can be produced from a variety of precursors via different processes. However, according to the survey, the supply chain for precursors is hard to trace. As the precursors have a substantial influence on the performance and cost of the products, producers tend to treat the precursor's type as proprietary technical knowledge. In some cases, the original raw materials of intermediate precursors, such as activated carbon and phenolic resin, are not traceable. Without information about the upstream supply chain of those intermediate materials, it is difficult to determine sustainability.

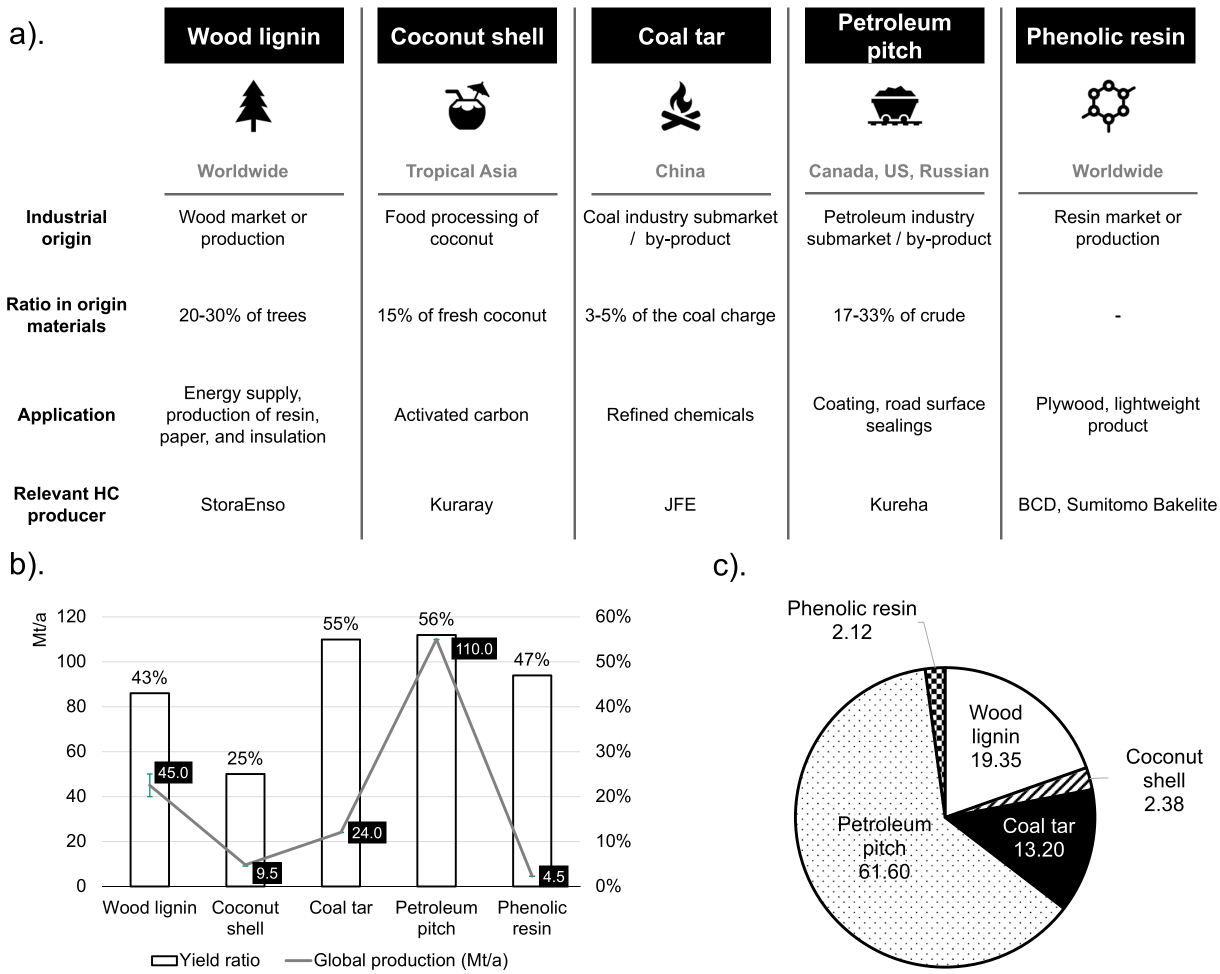

Fig. 3. Comparison of the common precursors for commercial HC products. a) General information about the origin, application, and HC producer [60–64]; b) comparison of the yield ratio (kg HC yield/kg precursor) and global production amount of the precursors [62,64–71]; c) production potential (Mt/a) of different precursors for producing HC anode materials based on global production and carbon yield of precursors. Overall production potential: 98.7 Mt/a.

3.3. *Economic aspects*

Consumers, manufacturers, and suppliers were consulted for the price of different commercial HC materials. Due to confidentiality, prices are presented in Fig. 4 without the corresponding product names. The price for the same product can widely vary depending on the purchased quantities. The suppliers and producers always mandate a minimum order amount when offering prices. It is typically much more

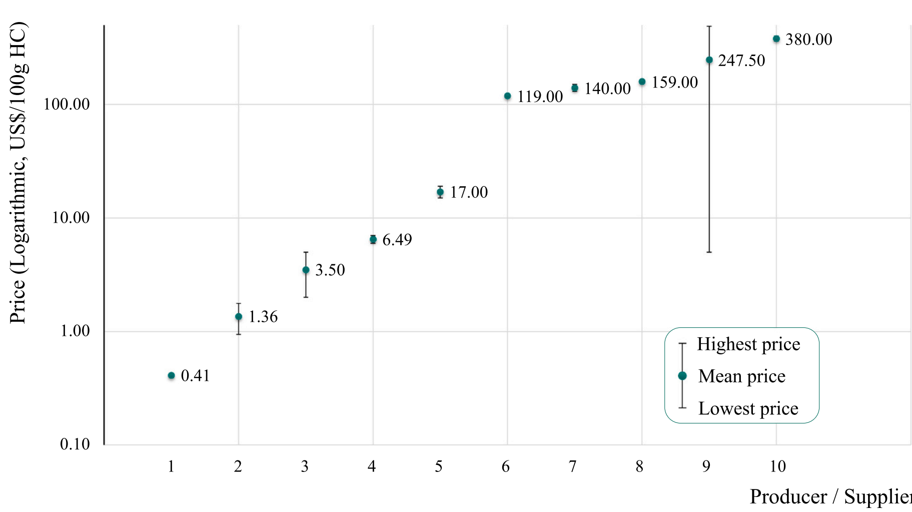

Fig. 4. Price variation for HC materials offered by different suppliers on the market. The mean values are calculated if sufficient price data is available. Otherwise single values are shown.

expensive when purchasing just a few samples as opposed to a fixed order quantity, which is normal for chemical items [76].

The prices obtained from the survey exhibit quite a broad range for 100 g HC, varying from 0.41US$ to 380US$. The price highly depends on the ordered quantity, the delivery distance, and quality (usually the specific capacity mAh/g offered by manufacturers). Precursors also have an impact on the performance and cost, and hence on the price of HC. However, due to a lack of data, this study cannot identify a correlation between theoretical capacity and pricing.

According to the expert survey, the price of ordering HC in large quantities is around 3.0 US$/100 g, significantly higher than the current market price of artificial graphite, which is between 0.4 and 1.5 US $/100 g, and natural graphite, which is in the range of 0.35–0.9 US $/100 g. It has been mentioned by Xie et al. [46] that the unmatured bulk production and initial application of HC contribute to the high price. Therefore, it is important to promote the mass production line of HC by coupling quality control with cost reduction and investigating the fabrication and structural characteristics.

Given the highly dispersed nature of the HC price and the absence of an official published price list, it is hypothesized that the HC market is still in its infant stage. Few producers, suppliers, and consumers are involved, leading to high prices, high uncertainty, and low transparency of market information. However, market information and data acquired from the literature and expert survey in this qualitative analysis is fragmented and prone to uncertainties. A further quantitative analysis-based evaluation is required.

4. Patent analysis of HC

4.1. Patent activity and intensity

352 patents (timeframe 1995–2021) were obtained from the patent search using the designed search terms, including 34 patents that refer to biomass and 44 patents that mention SIBs in the title.

In general, a low but continuous patent activity can be observed until 2012, with some small peaks. After 2012, patent applications began to increase, and after 2017 they accelerated significantly, as depicted in Fig. 5a. Note that the timeframe after 2019 is shaded in gray and not considered in the analysis, as explained in Section 2.2.2. The three most active countries in the HC field in terms of patent numbers are China (CN, 224 patents), Japan (JP, 103 patents), and South Korea (KR, 15 patents), which is in line with the patent study from IEA [77] and Baumann et al. [43]. These countries also show high activity in other fields of battery technology.

Eastern Asia countries have accumulated a sizable patent portfolio in the past 25 years. The need for anode materials has been fueled by the fast ramp-up of battery and electric vehicle production in eastern Asia. This region has been conducting in-depth research on anode materials ever since HC was first commercialized in Japan and produces the majority of the world's graphite due to low labor and energy costs, which has allowed for the development of facilities and experience that can be applied to HC anodes [78,79]. Japan dominated the patent activity of HC between 1995 and 2010. However, the rapid development of graphite-based LIBs presumably constrains the innovation potential and investment possibility for HC. Since 2011, as developments in electrolytes have significantly improved cycling performance, SIBs have gained more opportunities for commercialization. This has led to higher efforts for the R&D of HC-based electrode materials [42,80]. After 2016, more Chinese manufacturers have been involved in HC activities due to progress in the commercialization of SIBs. Since then, China has significantly boosted its patent filings.

Although the patent quantity is substantial, most of China's patents are national patents facing the domestic market, while priority patents and family patents that aim at the international market are lower than Japan. (Fig. 5b) A significant portion of national patents may indicate a low quality of the patents. As Chinese applicants are more driven by the synergies of patent applications (such as promotion, awards, or subsidy), rather than motives of innovation and global competence [81]. Japan has a more powerful international marketing strategy and aims to protect its innovations by filing family members in different countries.

The patent portfolio (Fig. 6) illustrates the share of HC patents in each country's national patenting activity and indicates the importance accorded to HC technology. China has the highest proportion, followed in decreasing order by Poland, Japan, and Korea.

Considering the economic growth and development state of the analyzed countries, as shown in Fig. 6, China and Japan exhibit a high patent intensity for HC technology regarding the national GDP (PPP) throughout the considered periods. In connection with the map of global manufacturers (Fig. 2), China and Japan have converted a part of the patent efforts into market action by launching commercial HC products, thus enabling these two countries to establish a dominant position in the current global market. This also supports the argument that solid patent activities might reflect substantial R&D expenditure and can promote market evolution [43,82]. Japan and China also have high growth in patent intensity, indicating possible upwards trends in research investment and increased technology knowledge acquisition. It has to be noted that there is a discussion regarding the quality of Chinese patents, making it difficult to derive a final conclusion [83,84]. Nevertheless, these two countries will likely maintain their target on the HC market in the near future. Poland, Korea, and the US follow in second place in

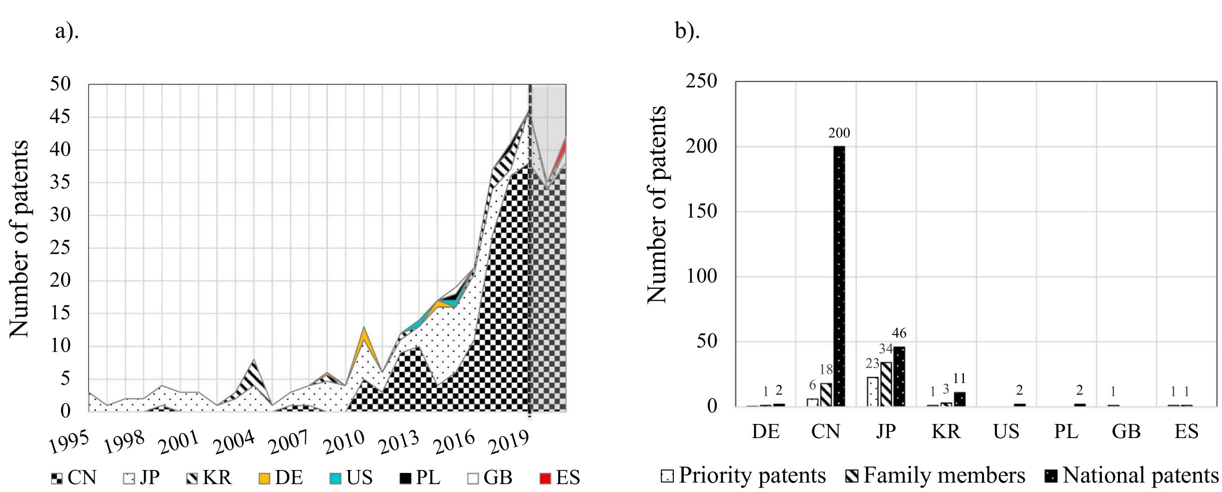

Fig. 5. a). Patent activity of 8 countries analyzed for HC anode materials between 1995 and 2021; b). Share of priority patents, family members, and national patents per inventor's home country for HC materials.

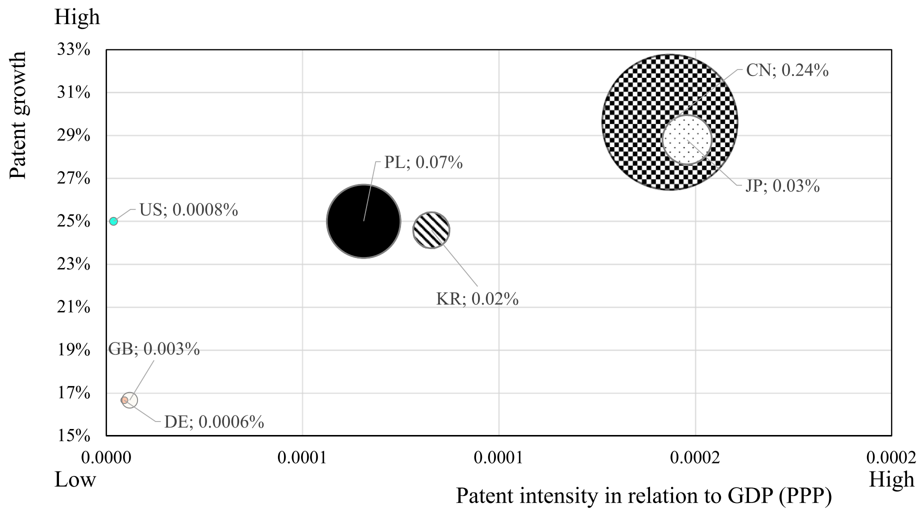

Fig. 6. Patent portfolio for HC anode materials. The annual average number of patents issued in the periods 2013–2015 and 2016–2018 are used to calculate the patent growth and intensity. The bubble size refers to the national technology share (also labeled by percentage number behind the country abbreviations). See Section 2.2.2 for details of the calculation.

patent growth. However, the US and Poland are experiencing rapid growth because they did not file any HC-related patents before 2016. This also applies to the UK. Due to a very low number of patents, the US, Poland, and UK are not included in the further discussion.

4.2. Innovation-market transfer

Applicants for HC patents were explicitly investigated to acquire more in-depth insight into the innovation-market transfer of the patents. Some producers, identified in Section 3.1, are highly active in patenting. (Fig. 7).

Shanshan is one of the most active patent holders; it has developed HC products for different battery types and established a mass production line. Kureha, another highly active company, invented the first commercial HC anode material, Carbonatron®, and has been active in filing HC patents for years. BTR and JFE have published patents since 2010, when HC almost disappeared, and the anode market was dominated by graphite [79]. The current HC manufacturers on the market, such as Bixidi, XFH, Best Graphite, and Sumitomo, are also actively involved in patenting.

Some companies active in patenting cannot be found in Table 1. The patents of those companies, such as Eliiy Power CO LTD, Kaijin New Energy, Yuhuang New Energy, Dongfang Electric Corp, and CPC Corp, have been filed in recent years since the SIB gained more momentum. However, SIBs have not been fully developed, and demand is still low, so they still have not gained enough driving force for pilot- or large-scale production.

In another case, it appears as though some companies with a history of strong patent activity have abandoned their efforts on this material and have lost interest in commercializing HC. Japanese enterprises, such as Sony, Hitachi, and Matsushita, fall into this scenario. Most of their patents date back to the early ages of battery development. There were

Fig. 7. Top Applicants of HC materials ordered by the number of patent applications. A darker block indicates more patent applications by the applicants. The country abbreviation is in square brackets under the applicant’s name, and the number represents the number of patents each applicant applied for.

many unknowns in the anode materials at the time. HC was one of several materials considered by these companies when designing anodes for commercial LIBs. Later, their investment in HC gradually shifted to graphite [79,85].

No information on HC-related patents was found in the two European countries where the HC pilot- and mass production lines are located, i.e., Finland and Sweden. It might be that these companies have not filed patents for their technologies. Given the high mobility of technical knowledge and scientific research inside the EU, probably the R&D is collaboratively conducted by European countries. Knowledge and innovation may be transferred from one country to another. By integrating the market analysis results (Section 3), it is reasonable to infer that despite a low rate of patent filing, Europe has accumulated innovation and know-how in HC technology, especially in biomass-based HC.

However, patents can only convey a country's R&D effort to a certain extent, rather than the entire picture. Not all patents originate from genuine innovation, and vice versa, not all technological advancements are patented. Only a portion of R&D spending can yield innovations, and only a part of the R&D findings and inventions can be brought into the market [43].

To better understand the relationship between universities, industry, and innovation in HC, the applicants' types in each country are distinguished, as displayed in Fig. 8. Many Chinese universities are actively engaged in HC patenting. This is assumed to be related to the performance evaluation process of the Chinese education system, where patenting can play a positive role, and thus it drives more people to apply for patents based on research outcomes [86]. Moreover, it has been suggested by Fischer et al. [87] and Baumann et al. [43] that there are many incentives for patenting in Chinese universities, including subsidies and reducing costs for patenting, which may lead to an increase in the number of filings, but not necessarily the quality. Further investigation is needed to determine the value of Chinese HC patents.

4.3. Technological life cycle (TLC)

The development of technology is divided into four stages, also known as the technology life cycle: emerging, consolidation, market penetration, and maturity (Fig. 9a). In the emerging stages, the technology begins to generate interest and initiate R&D activities. Consolidation occurs when the technology has accumulated a certain level of R&D experience but has not yet formed a commercial market or has failed to meet expectations. There may be fluctuations (hype phase) throughout this period, due to inflated publicity in the early market gradually cooling and doubt about the performance of the new technology. Following this, the R&D of the technology enters a phase of rapid expansion, which implies that more participants are involved in the market, and R&D efforts are enhanced, leading to so-called market penetration [49]. After reaching the peak, it enters a maturity phase, and as the technology gains commercial success, patent activities will gradually decline.

The patent data can be used for technological estimation and forecasting, as the annual patent application profile mirrors the so-called S-curve of the four stages of technology development [49]. The approximated TLC analysis draws a development picture of HC technology. A fitting formula is proposed for a technical learning curve of HC that matches the theoretical TLC by a 6th-degree polynomial trend based on the aggregated number of patents throughout the years (Fig. 9b). From this, it can be observed that the development of HC is undergoing an acceleration. However, it is hard to identify if the technology is in a hype phase or a market penetration phase. The future development of HC is closely related to SIBs. The technical bottlenecks (i.e. low capacity, cycle stability) of SIB need to be overcome for commercialization in the future. On the other hand, the production routes and supply chains also need to be continuously optimized to exploit the cost and supply advantages of SIBs.

Moreover, the keyword search with designed terms yields only 352 HC-related patents. Unlike previous patent studies [42,43,82] that fit the TLC with a significantly higher number of patents, this small quantity makes it difficult to determine the technology life stage approximated through TLC.

5. Conclusion and outlook

This study combines literature analysis and expert survey with patent analysis to investigate the present development of HC materials from technology, market, and innovation perspectives. The approach blending the qualitative information and quantitative results allows this study to gain an overview of the situation and future trends of HC technology. As a result, it offers an informative base for future research and industrial development of HC and enables proposing necessary actions to avert prospective difficulties.

Compared to graphite, HC has an abundant choice of precursors, more potential to reduce production costs and environmental impacts,

Fig. 8. Distribution of patent applicants by type in different countries of residence, normalized by the total number of HC-related patents in each specific country. Numbers written in bars represent the actual number of patents.

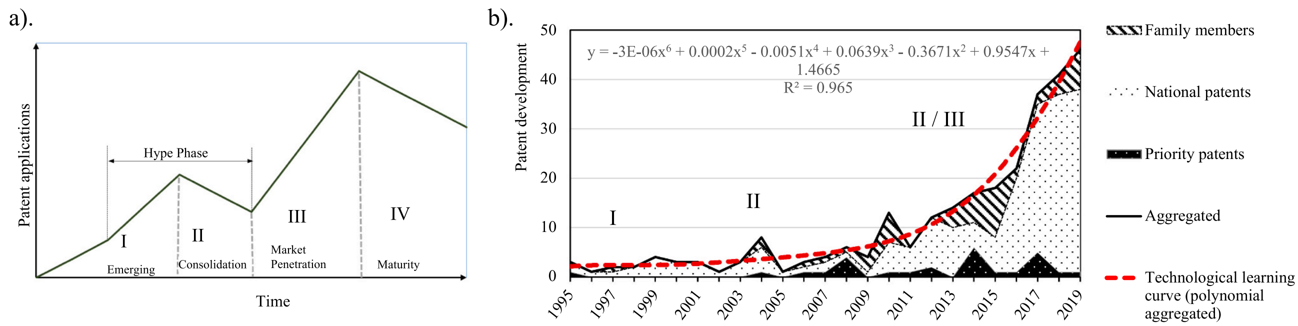

Fig. 9. a). The number of patent applications for different stages of the technological life cycle; b). Technological life cycle (TLC) stage of HC anode materials approximated (6th-degree polynomial regression) based on the yearly published number of all patents applied for.

and higher capacity for sodium-ion storage. HC also poses suitability for low-temperature and high-power applications. It can be concluded that HC is currently the most advanced and promising anode option for SIBs. However, as an anode material built in the same period as graphite, market activities of HC are relatively limited. The re-emergence of SIBs in recent years is a driving force contributing to increased patenting activities of HC.

According to the patent analysis, the technology development of HC is accelerating, but the maturity level is still low. At this stage, no established HC manufacturing path for mass production is available. Many producers claim that graphite production equipment may easily be adapted for HC. However, it is unclear if a technical threshold exists for processing the raw materials. Cell performance can be significantly affected by minor modifications to the HC's microstructure, which stems from the precursors and their processing. Therefore, the consistency of raw materials and further processing are very important factors, and the final R&D investment may be higher than expected.

The R&D and commercialization of HC have taken place in some countries. China and Japan can be considered technology leaders at this moment, in terms of their current manufacturing capacities and patent activities. In other regions, such as Europe and the U.S., more R&D investment and more efficient commercialization of innovations are expected for HC. Up to now, the demand for HC is still volatile, which leads to uncertainty on the supply side and corresponding price fluctuations. Due to the small number of patents, it is difficult to determine if HC is going through a hype cycle. The development of SIBs has a direct impact on how HC markets will evolve in the future. Despite strong motivation from market participants, there is a possibility that the HC boom will subside after the marketing hype, especially considering the potential technical threshold and the uncertainty evident in the current market both for SIBs and HC.

Different precursors of HC are investigated in this work, including their production potential, environmental impacts, and cost, to identify which are more suitable and sustainable for mass production. This screening should be performed as early as possible, before the precursors are introduced into large-scale plants. Information traceability of raw materials should be promoted for positive and sustainability-oriented market development. For future development of HC, it is suggested that more transparency of the upstream supply chain, cost reduction, and environmental consciousness throughout the entire life cycle are required in order to achieve a mature market and sustainable commercialization of HC technology.

Abbreviations

CMC	carboxymethyl cellulose
CPC	cooperative patent classification
DLC	diamond-like carbon film
EPO	European Patent Office
EU	European Union
GDP	gross domestic product
HC	hard carbon
IEA	international energy agency
IPC	international patent classification
KIB(s)	potassium-ion battery(-ies)
LIB(s)	lithium-ion battery(-ies)
OPS	Open Patent Services
PPP	purchasing power parity
PVDF	polyvinylidene fluoride
R&D	research and development
SBR	styrene-butadiene rubber
SEI	solid electrolyte interphase
SIB(s)	sodium-ion battery(-ies)
TLC	technological life cycle
US	United States

Math formula

$P_{HC,\ t}$	patent number of HC related technology in concerned timeframe t
$P_{a,\ t}$	total national patent number in concerned timeframe t
$GDP_{PPP,\ t}$	gross domestic product in accordance with purchasing power parity PPP in concerned timeframe t.
$NTS_{HC,\ t}$	national technology share of HC in the concerned timeframe t
$Pg_{HC,\ t}$	HC patent growth in the timeframe t with regard to t-1
$Pi_{HC,\ t}$	patent intensity of HC regarding to the $GDP_{PPP,\ t}$
M_i	annual production amount (Mt/a) of raw material i worldwide
Y_i	yield amount (kg) of hard carbon produced 1 kg raw material i
$P_{i,\ t}$	annual maximum production potential (Mt/a) of HC from raw material i
cl	search term represent for classification (including IPC and CPC)
pd	search term represent for publication date of the patent
ti	search term represent for title

CRediT authorship contribution statement

Huiting Liu: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Manuel Baumann:** Conceptualization, Methodology, Software, Formal analysis, Writing – review & editing, Supervision. **Xinwei Dou:** Validation, Investigation, Writing – review & editing. **Julian Klemens:** Validation, Investigation, Writing – original draft. **Luca Schneider:** Validation, Investigation, Writing – original draft, Visualization. **Ann-Kathrin Wurba:** Validation, Investigation, Writing – original draft. **Marcel Häringer:** Validation, Investigation, Writing – review & editing. **Phillip Scharfer:** Supervision, Funding acquisition. **Helmut Ehrenberg:** Writing – review & editing, Supervision, Funding acquisition. **Wilhelm Schabel:** Supervision, Funding acquisition.

Jürgen Fleischer: Supervision, Funding acquisition. **Niklas von der Assen:** Conceptualization, Writing – review & editing, Supervision. **Marcel Weil:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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

Data that is not confidential will be made available as request.

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Appendix A. Supplementary data

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