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Introduction: The Future of Carbon Materials – The Industrial Perspective

Hubert Jäger[1]*, Wilhelm Frohs*[2]*, and Tilo Hauke*[2]

[1] *Technische Universität Dresden, Institute of Lightweigth Engineering and Polymer Technology (ILK), Hohlbein Street 3, Dresden, 01307, Germany*
[2] *SGL Carbon GmbH, Werner-von-Siemens-Street 18, 86405 Meitingen, Germany*

1.1 Overview

This chapter provides information about the industrial importance of various carbon and graphite materials. Carbon and graphite materials are mostly unknown to the public. They are obvious in few consumer products only, such as lead pencils, or in sporting goods as carbon fibers, for example.

In contrast, the importance of carbon materials for the production of iron, steel, and aluminum is not common knowledge. The iron, steel, and aluminum industry created in 2011 a global market value of around 1100 billion €. This is equivalent to around 50% of the value of the global annual crude oil production. Although we will not consider metallurgical coke in this chapter, the market value should be mentioned; it is around 155 billion €. Also not considered here are carbon black (11 billion €) and activated carbon (1.8 billion €). The market value of carbon materials in total (without metallurgical coke) is at around 42 billion € (Figure 1.1). The biggest contributor with a market value of 18 billion € is carbon anodes for aluminum electrolysis. Within the group of polygranular carbon materials, the anodes are followed by graphite electrodes for the production of electric arc furnace (EAF) steel with a market value of six billion €. Smaller markets are cathodes for the production of aluminum (1.4 billion €), fine-grained graphite for multifold applications (0.7 billion €), furnace linings for blast furnace steel production (0.3 billion €), and carbon electrodes for the production of silicon (0.2 billion €). Other carbon materials like natural graphite, carbon fibers, and graphite for Li-ion batteries play a minor role versus the conventional carbon products yet. Changes may happen in the near future driven by the need for the efficient storage and use of energy. The market for conventional carbon materials will continue to grow driven by the demand coming from the BRIC countries (Brazil, Russia, India, and China).

New forms of carbon, the carbon nanomaterials, created huge expectations but are currently not produced in an industrial scale with the exception of multiwall carbon nanotubes (MWCNTs). With the recent demonstration of the potential

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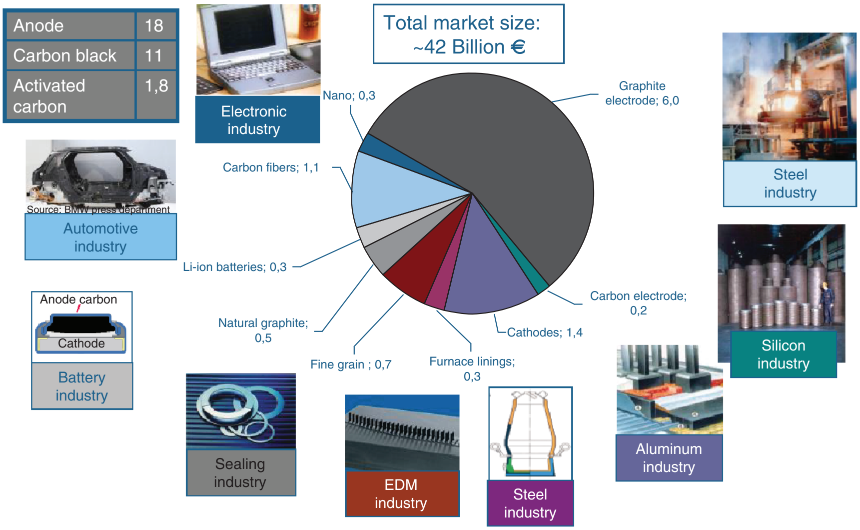


Figure 1.1 Carbon materials and their market value.

of graphene, a single graphite layer, in microelectronic circuits, we might see the beginning of a new market for carbon materials.

1.2 Traditional Carbon and Graphite Materials

Traditional carbon materials that are considered in this chapter are:

- Graphite electrodes for melting of steel scrap.
- Carbon electrodes for silicon production.
- Cathodes for the aluminum electrolysis.
- Furnace linings for blast furnaces.
- Fine-grained graphite for silicon production, machining, and others.

With the availability of stable electrical power networks, the electricity was used for heat generation and electrochemical industrial processes. Moisson demonstrated the first steel production with an EAF in 1891. The first EAF plant started its operation in 1906 (Remscheid, Germany). Simply baked carbon electrodes most probably with anthracite and carbon black as filler were used. The electrode diameter was small. In the 1920s more and more electrodes were used, which had been graphitized. The production of EAF steel grew to around 20 million t in 1950. After 1950 the production of EAF steel developed rapidly and exceeded 100 million t in the 1970s. The raw material in this time period was often pitch coke produced by chamber coking. Special coke grades, so-called needle cokes, produced in the delayed coking process of crude oil refineries were developed later in 1960 and commercialized in 1970. This development represented a quantum leap in the quality of graphite electrodes. The most frequently used electrode became an electrode with 600 mm in diameter. As a consequence, there was substantial progress in the stability and efficiency of the melting process. The average consumption of graphite electrodes was reduced to below 4 kg/t steel. Further improvements in raw material quality, graphite electrode processing, furnace technology, and steelmaking process regulations reduced the graphite electrode consumption to about 2 kg/t steel in average (Figure 1.2). In particular the water spraying on top of the furnace roof was a genius idea to reduce significantly the graphite consumption due to oxidation. The lowest graphite consumption figure achieved so far was 0.74 kg/t with an electrode with a diameter of 800 mm on a direct current (DC) furnace.

Graphite electrodes are produced in mostly all continents. Traditional graphite electrode producers are GrafTech International, the SGL Group, and the Japanese producers Tokai, SDK, and Nippon Carbon. Later electrode producer followed in India and recently in China (Figure 1.3).

The production of EAF steel reached about 550 million t in 2020. Much stronger was the growth in blast furnace steel (Figure 1.4). This situation was

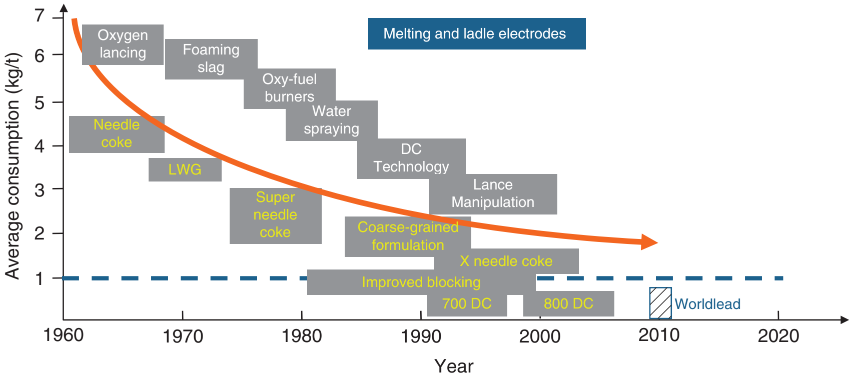


Figure 1.2 Development of the specific consumption of graphite electrodes.

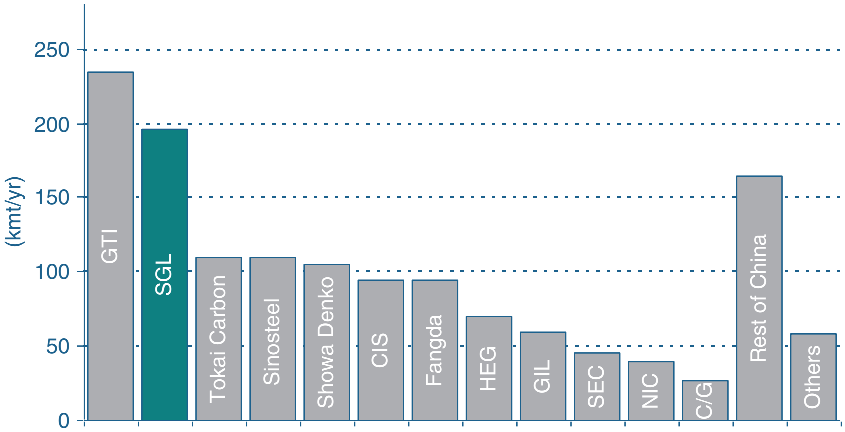


Figure 1.3 Graphite electrode producers and their production capacity (2018). SGL: Since 2017 Showa Denko.

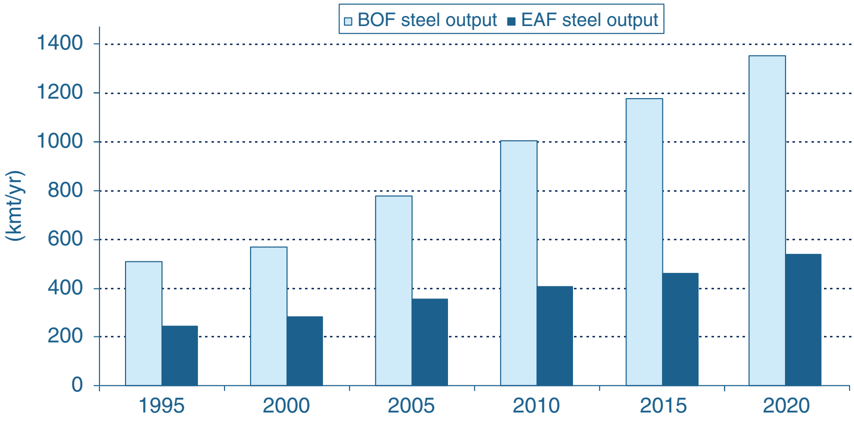
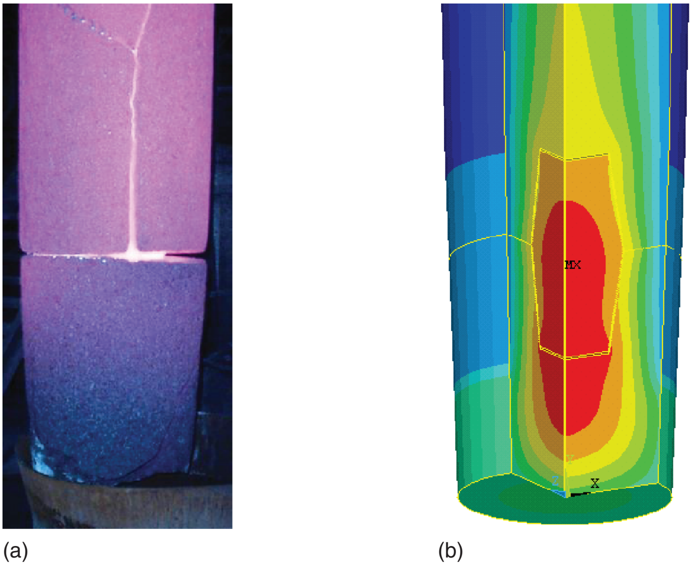


Figure 1.4 Blast furnace and EAF steel production.

created by the economic growth in China, which, as a young economy, is suffering the steel scrap required for EAF process. This will change over the times and the EAF process will pick up.

Graphite electrodes are exposed to extreme conditions during the melting of steel. From a tip temperature of several thousand degrees centigrade, the temperature falls to about 1000 °C close to the roof of the furnace and to a few hundred degrees centigrade on top of the roof. Lengthwise and transversal temperature gradients create extensive thermal stresses. These high stresses initiate material cracks that can lead to severe material losses during the melting process (Figure 1.5).



(a) (b)

Figure 1.5 Graphite electrode. (a) Graphite electrode with crack in the joint area. (b) Finite element simulation of temperature distribution.

The biggest disadvantage of these graphite losses is the expensive interruptions in the steel production chain. Thus the efforts of the graphite electrode producers focused on the minimization of these losses by the use of improved raw materials improved the process consistency, impacting the thermal compatibility between the connecting pin and the graphite electrode. These are only some approaches to minimize material losses and to enable a high efficiency of the scrap melting process. Although graphite electrodes have been produced since almost hundred years, the complete understanding was never accomplished.

Carbon electrode means a solely baked and not graphitized electrode composed of calcined anthracite and or synthetic graphite. These prebaked electrodes are an alternative to the Söderberg electrodes, a green paste that is baked and graphitized during its application in the EAF. Carbon electrodes reach diameters up to 1400 mm (Figure 1.6). They are mainly used for the production of metallic silicon and phosphorus. Notably the production of silicon doubled in between 1990 and 2010 (Figure 1.7). The strongest driver was the solar industry.

Figure 1.6 Carbon electrodes with diameters up to 1400 mm.

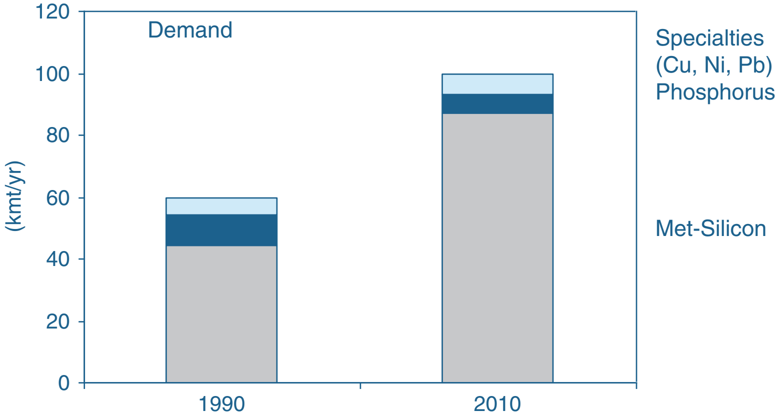


Figure 1.7 The demand for carbon electrodes.

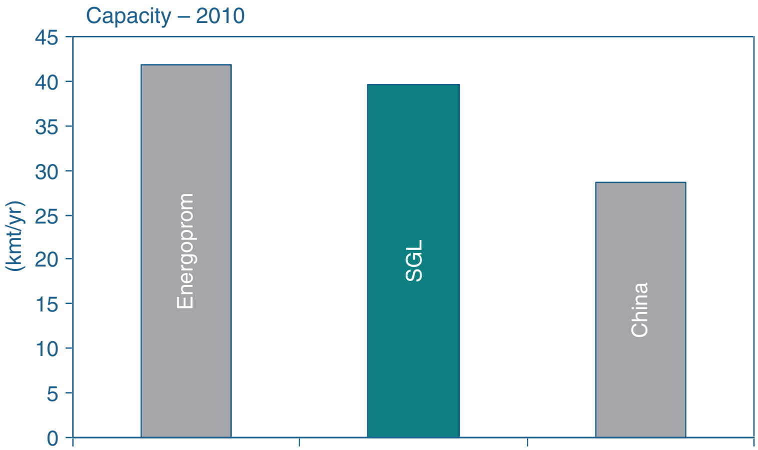


Figure 1.8 Carbon electrode producer and capacity. SGL: Since 2018 COBEX.

The number of carbon electrode producers is rather small (Figure 1.8). The estimated carbon electrode production capacity is slightly above the demand. This free capacity will soon be covered as the demand for silicon will further grow with the ongoing installation of solar panels. As in the case of graphite electrodes, the customer expects a smooth operation without excessive consumption.

Cathodes build the bottom of the Hall–Héroult electrolysis cell for the production of primary aluminum. This process was developed in 1886 and is still unchanged in its basic principles today. Alumina is reduced in a cryolite bath electrochemically to elemental liquid aluminum (Figure 1.9). The electric current

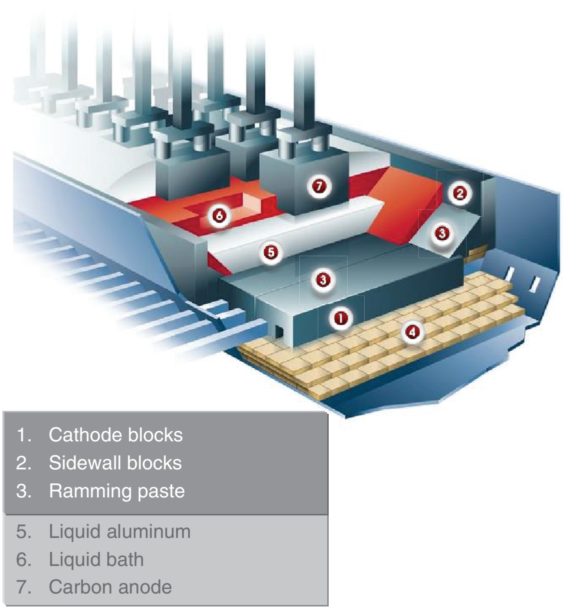


Figure 1.9 Aluminum electrolysis cell.

passes through the bath to the anode electrode on top of the cell. The anodes were consumed during this electrochemical process and react to CO_2. The anode consumption per ton of aluminum is in average 0.47 t. For the production of 41 million t of aluminum in the year 2011, the demand for carbon anodes is 19.3 million t. Aluminum is strongly growing with an expected annual rate of about 8% in 2011 and the following years. One main driver is the automotive industry to replace steel components for lightweight construction.

Due to the design of the electrolysis cell, three types of cathodes are in use. The old cathode type is the amorphous type consisting mainly of calcined anthracite and is solely baked. Graphitic cathodes contain a high content of synthetic graphite and are also solely baked. The graphite cathodes are made from coke and are graphitized to a definite temperature. This temperature provides the desired electrical and thermal conductivity. It is needless to say that the demand for cathodes was growing in the last decades (Figure 1.10). All grades did benefit but by far the strongest growth was noticed for graphite cathodes. Cathode producers are located in Europe, Japan, Russia, and China (Figure 1.11).

The main reason for the existence of the different types of cathodes is the height of the applied electrical power. The increase in amperage over the years is shown in Figure 1.12. The market introduction of graphite cathodes happened in the 1970s and enabled with its lower electrical resistivity the further increase in amperage and thus improved the efficiency of the cell. In spite of being an old process, many efforts are ongoing to drive the production of aluminum on the edge in productivity, durability of the cell, and energy efficiency. New processes that are under development are coatings with TiB_2 to improve the wettability

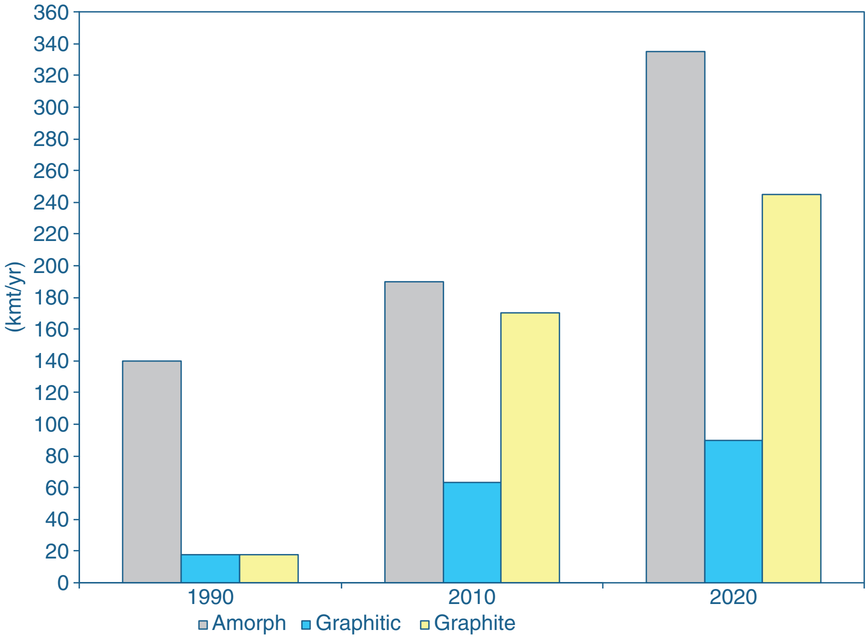


Figure 1.10 Cathode production by grade.

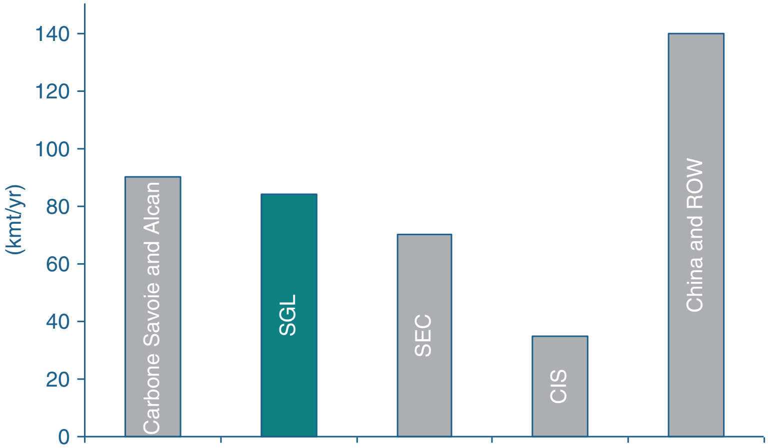


Figure 1.11 Cathode producers and their capacity. SGL: Since 2018 COBEX.

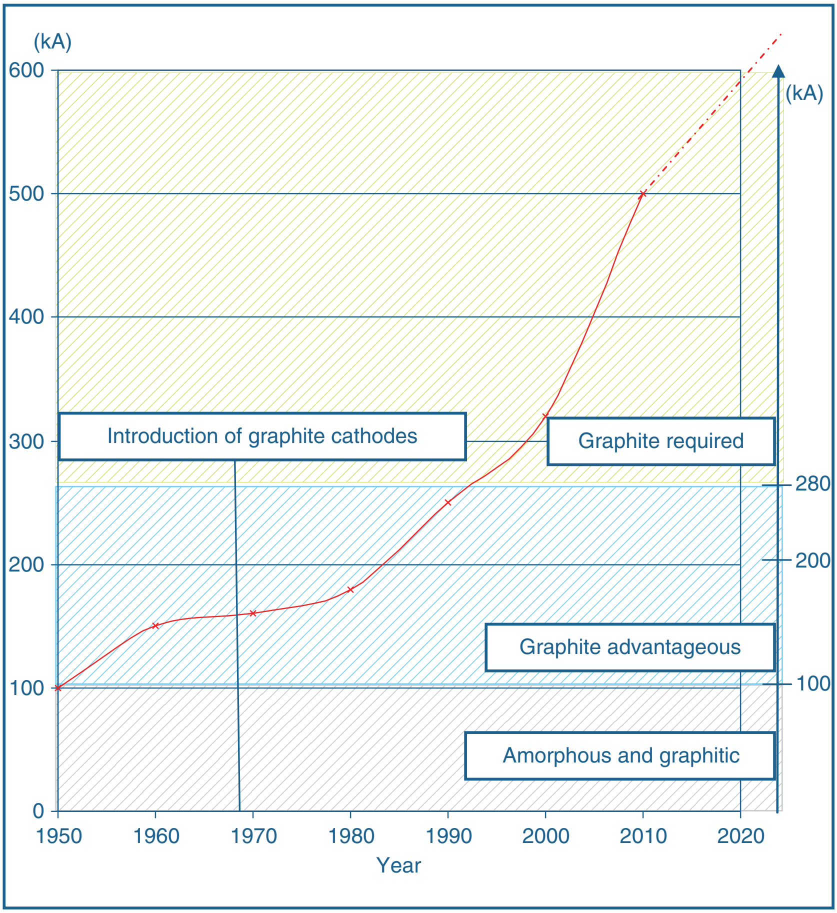


Figure 1.12 Increase in cell amperage over the last 70 years.

of carbon by the liquid aluminum. The drained cell design should reduce the distance between the cathode bottom and the anode above. The target is to improve the stability of the current flow and thus to increase the cell efficiency. The carbothermic process is a direct reduction of alumina by carbon under heat. All efforts to replace the anode by a so-called non-consuming inert anode failed so far. The bath conditions are so severe that no other material than carbon was yet demonstrated to survive.

Carbon and graphite bricks are used to construct the hearth of a blast furnace and basic oxygen furnace (BOF) for the production of iron and steel. Carbon and graphite materials are first choice in a chemically aggressive environment at high temperatures (Figure 1.13). The demand for blast furnace steel was consistently growing on a global basis, but the regional developments are different (Figure 1.4). The growth flattened in the 1970s in the Western economies including Japan. The growth happened from there on in Asia, first went to South Korea, then to China,

Figure 1.13 Test assembling of a blast furnace lining.

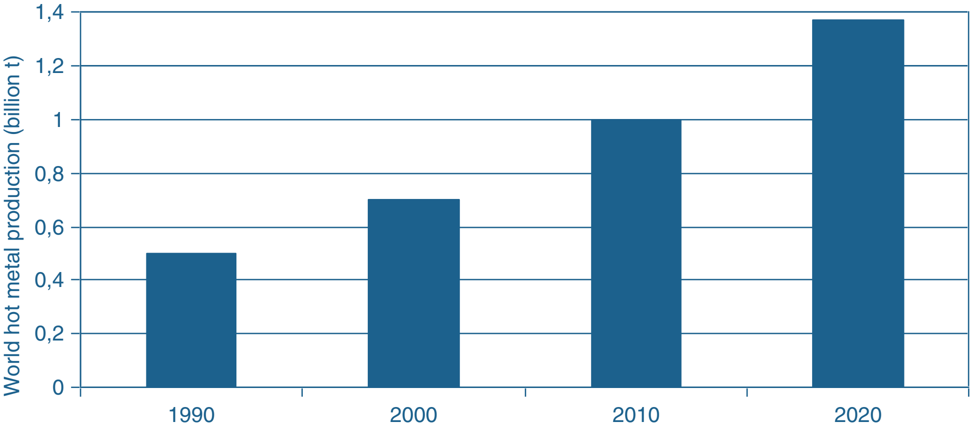


Figure 1.14 Hot metal production in blast furnaces.

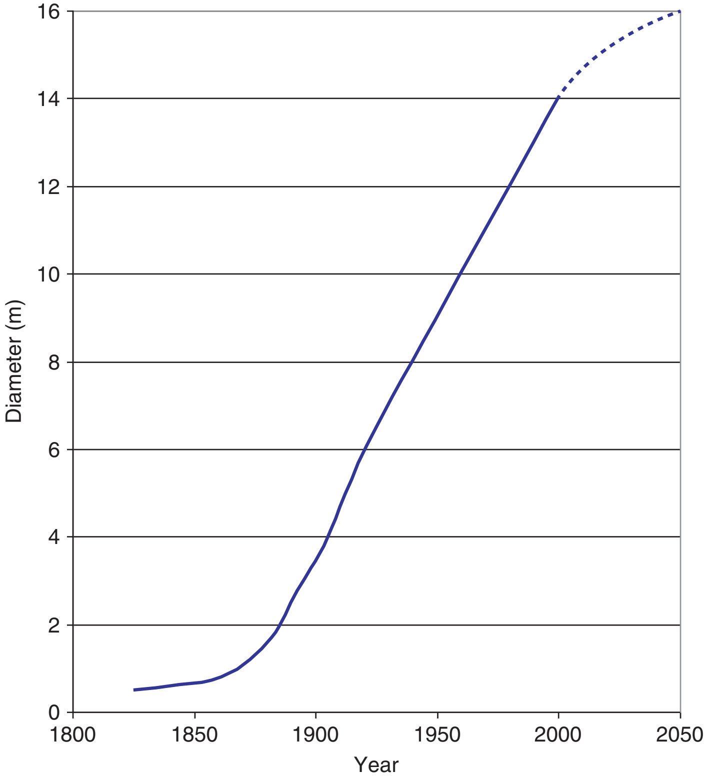


Figure 1.15 Blast furnace diameter.

and later to India. The production capacities for furnace linings are located in Germany and Japan, as well as in China and Russia (Figure 1.14).

Over the last 20 years, the increasing BOF steel production was achieved with fewer furnaces. The furnace size also referred to as the diameter of the heart increased from a few meters up to 15 m (Figure 1.15). Today a single blast furnace produces about four million t of liquid iron annually. The lifetime of the lining reaches typically 12–15 years, but in few cases 20 years have been demonstrated with a production of 60 million t iron during such a campaign. It is evident that the steel companies are very conservative in changing lining concepts or the grades of the lining material. Challenge is the chemical erosion caused by the interaction between the liquid iron and the carbon material. One improvement in the recent past was the introduction of so-called microporous linings with mainly pores below 1 μm in diameter. The right selection of anthracite can significantly elongate the lifetime of the furnace cycle. Hence, best chemical resistance and mechanical wear resistance are the goals for development.

So far we have considered coarse-grained carbon and graphite materials. Specialty graphite is a polygranular material with very fine grain sizes. To achieve a high isotropy, not only the raw material is carefully selected among isotropic cokes, but also the process of forming by isostatic pressure application supports

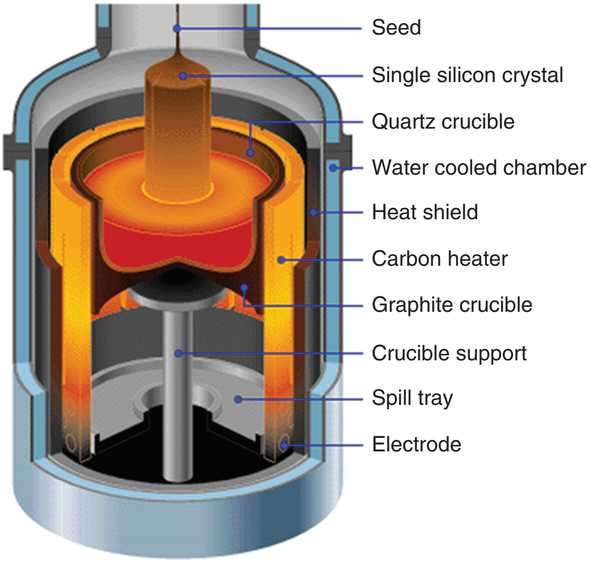


Figure 1.16 Silicon single crystal production.

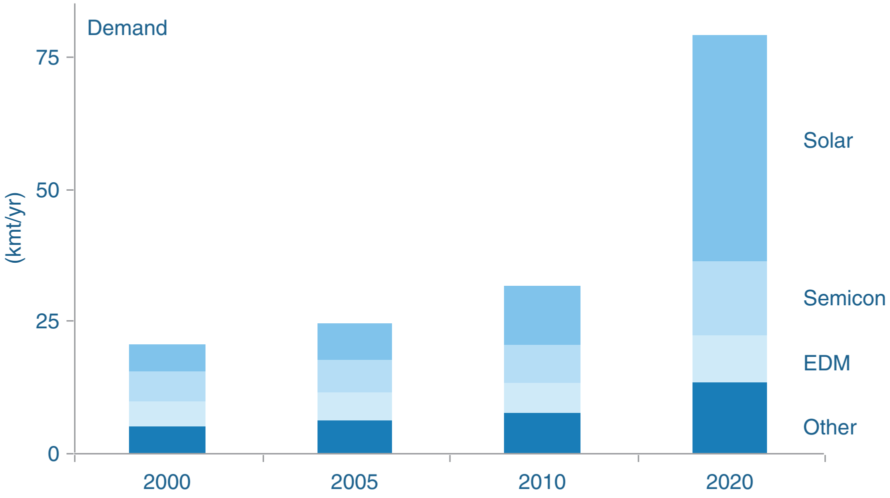


Figure 1.17 Demand for fine-grained graphite.

the isotropy. This graphite material is known as iso-graphite. Its main application is the production of silicon single crystals (Figure 1.16) for the semiconductor industry and the production of polysilicon for the solar industry (Figure 1.17). Other applications are electrical discharge machining, casting of non-iron metals, and many other applications.

The main production capacities are located in Japan (Figure 1.18). China entered this market recently and strives to become a serious competitor in this field.

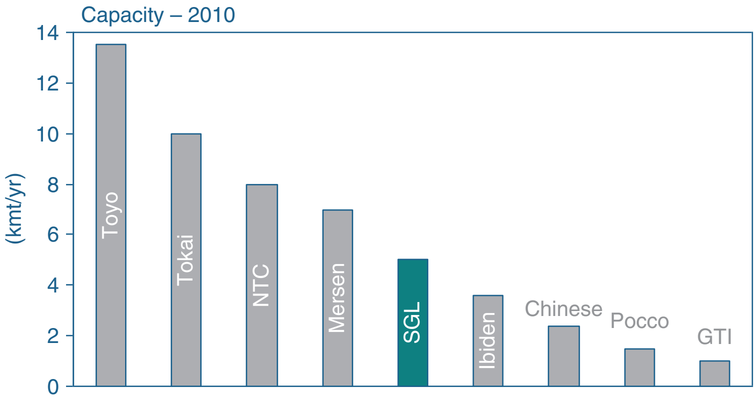


Figure 1.18 Fine-grained graphite producer.

The mechanical strength is the key quality parameter for iso-graphite. Fundamentally the strength of graphite increases with decreasing grain size. This led to a decrease in grain size during the last decades to nowadays few microns and mechanical strength of up to 100 MPa. The future challenging task is the process technology and automation to produce bigger block sizes at high process yield.

It was shown that traditional carbon and graphite materials have a long-lasting history. During this history they have improved their quality and reliability. Their consumption in their respective application was reduced. Despite this long history there is still room for improvement and open questions for basic research. The industrial perspectives for these materials are prosperous. The most probably ongoing growth in the BRIC countries will provide a constant grown in the demand for graphite electrodes, cathodes, and furnace linings. Iso-graphite will benefit from the global expansion of clean solar energy.

1.3 Modern Application of Carbon Materials

Carbon fibers are thin (diameter = 7 μm), light (real density = 1.8 g/cm^3), strong (strength up to >6 GPa), and stiff (Young's modulus up to 900 GPa) (Figure 1.19). These fibers exceed any other fiber material in its specific properties and come close to the theoretically predicted properties of pure graphite. The properties depend on the temperature weakly only. Only the presence of oxygen limits the application at elevated temperatures. Carbon fibers can be made from different fiber precursors. These fiber precursors can be polyacrylonitrile (PAN), pitch, or rayon. During the history of the carbon fiber development, PAN-based carbon fiber won the race. Reasons had been the relatively easy processing and the wideness of achievable mechanical properties. Mesophase pitch-based carbon fibers are only competitive in applications with extreme stiffness. Embedded in a polymer matrix (carbon fiber reinforced polymer [CFRP]) or a carbon matrix (carbon fiber reinforced carbon [CFRC]), superior material properties are the outcome. These spectacular properties were soon recognized for military application, an

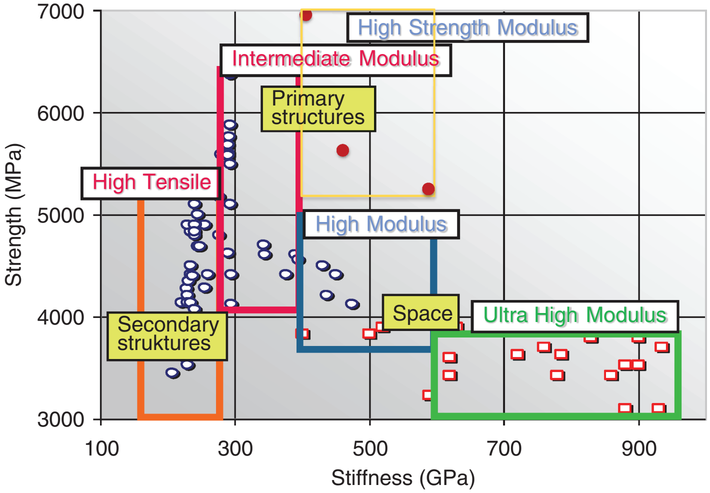


Figure 1.19 Mechanical properties of carbon fibers.

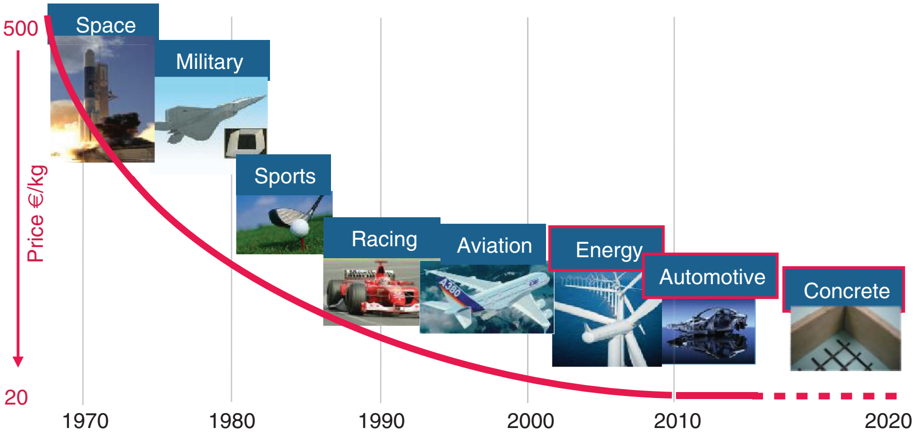


Figure 1.20 Carbon fiber fields of application.

area where functionality overrules cost (Figure 1.20). As the carbon fiber price dropped, application in sport articles followed. Today carbon fibers are common in the civil aviation industry. Weight and thus the reduction of operational cost made the use of CFRPs' attractive.

Modern planes will contain more than 50% of their constructional parts made from CFRPs. In the area of wind power, the blade length is going to exceed 70 m. To provide the necessary stiffness to these blades, the application of CFRPs is unavoidable. CFRPs are indispensable for the requested energy saving in transportation and the start into e-mobility. These new markets will cause a heavily increasing demand for carbon fibers (Figure 1.21). Forecast expects a growth in demand from 20 000 t in 2010 to 270 000 t in 2030. The production know-how (precursor) and production capacities are concentrated in companies based in

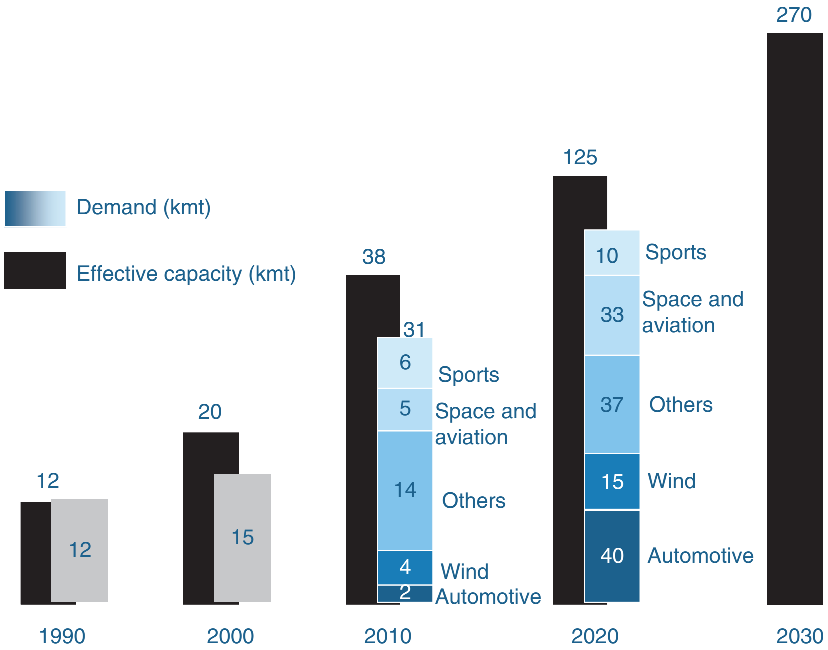


Figure 1.21 Carbon fiber demand and capacity.

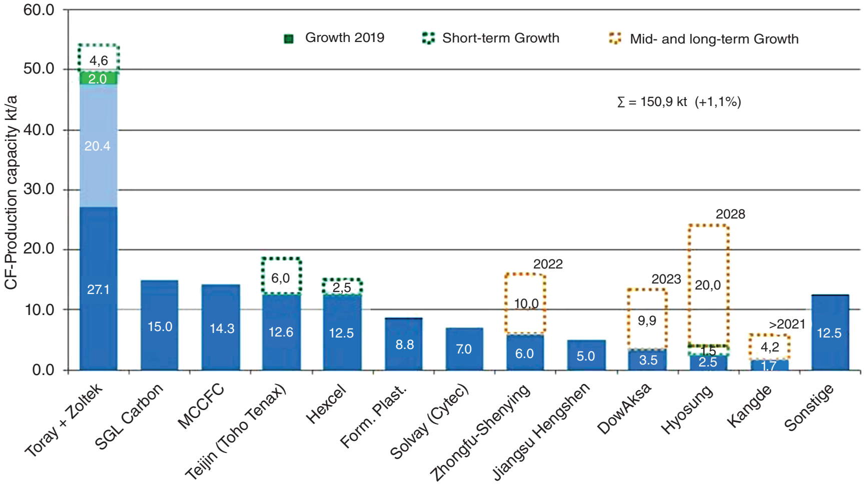


Figure 1.22 Carbon fiber producers and their estimated capacities. Sources: The Global CF and CC Market 2018, Sauer & Kühnel; Annual Report Composites United 2019).

Japan or the United States (Figure 1.22). Europe started to establish its own independent position in this market.

The production cost for CFRPs has to be reduced to become competitive versus the traditional construction materials steel and aluminum. The cost for carbon fibers production is linked to the oil price and energy pricing; the biggest potential

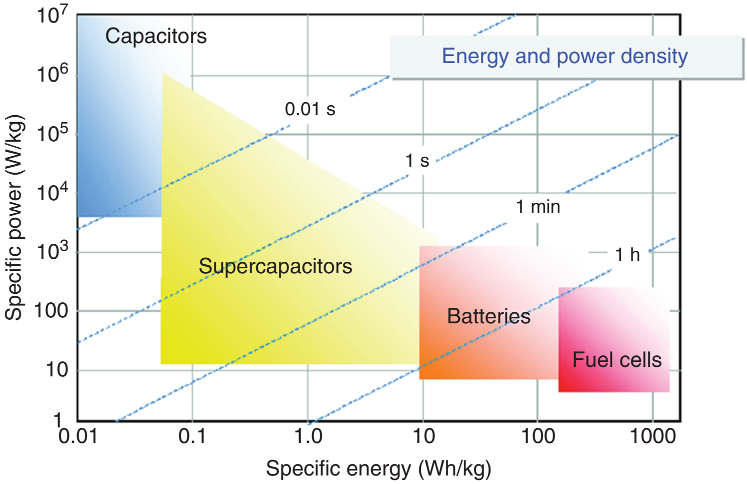


Figure 1.23 Energy and power density for different storage systems. Source: R. Kötz, M. Hahn, R. Gallay, 9th UECT-Ulm, Electrochemical Talks, 2004, Neu-Ulm, Germany.

today is in the manufacturing process for CFRPs itself. Automation and reasonable lot sizes are the keys to success. The development of matrix systems that will accelerate the manufacturing processes and enable the recycling into new components is necessary. Thermoplastic polymers will partially replace the currently used thermosetting resin systems. The fiber surface has to be modified to provide the required interaction with the respective polymer system. On a long-term perspective, precursor fibers based on renewable materials and “green” matrices will be the answer to the current CO_2 footprint discussions. All this needs big efforts in research and development.

Lightweight construction is one precondition for the breakthrough of e-mobility. Another challenge is the storage of electrical energy. Different storage systems are available or under development. Due to their differences in power density and loading and unloading characteristics, the intelligent combination of all of them is necessary. This could provide the desired acceleration and cruising range (Figure 1.23). Capacitive systems with fast unloading enable the powerful acceleration: Li-ion batteries will cover the midsize cruising range, and fuel cell system will provide the energy for longer distances. In all these systems that are available or under development, carbon materials play an essential role.

The anode in Li-ion batteries is made from graphite. The electrical characteristics are determined by a bunch of parameters, from the raw material source toward processing temperatures, grain shaping, coating, and many others. Natural graphite-based anode material provides good charging and discharging characteristics. An advantage of natural graphite versus synthetic graphite is the unneeded graphitization treatment. A forecast for the expected demand for Li-ion batteries storage capacity is shown in Figure 1.24.

As in many other cases the know-how and production capacity are located in Japan (Figure 1.25). Europe with its high end car industry did hard to invest into this development. Currently, Europe is struggling to catch up.

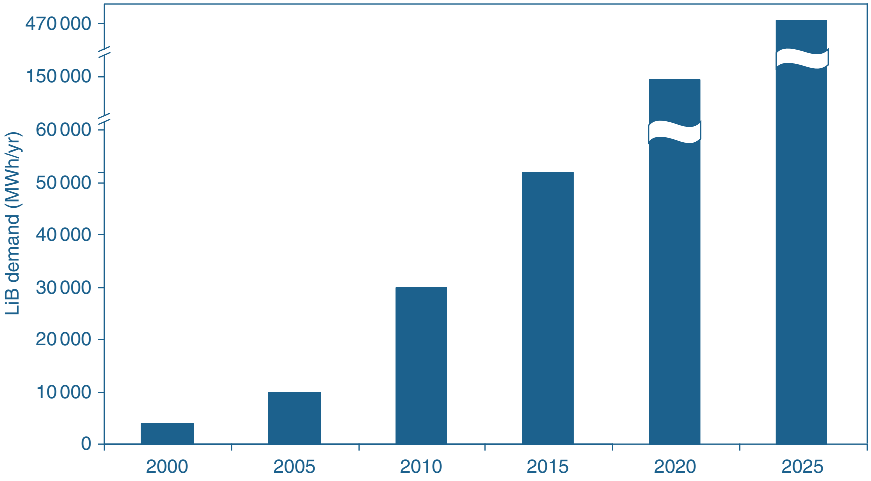


Figure 1.24 Expected Li-ion battery demand. Sources: H. Takeshita, IIT, 25th Int. Batt. Sem and Exhibit. Fort Lauderdale, FL, USA, 2008; Next-mobility news 09/2017; Roland Berger Study on LiB /2018.

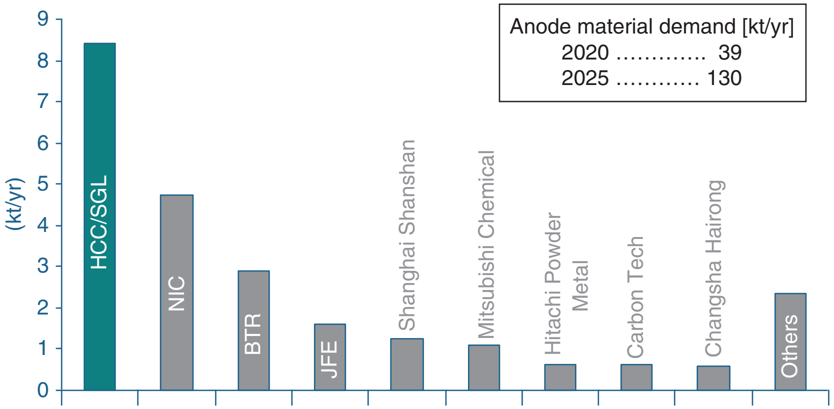


Figure 1.25 Li-ion anode material producer and their capacity.

Electrical discharge layer capacitors (EDLCs) are fast loading and unloading systems. In contrary to the Li-ion batteries, in which the intercalation in between the graphite layers is the storage process, EDLCs require an easy accessible high surface area with a preferred porosity in the nano-range for the adsorption/desorption of charge carriers. Suitable carbon materials can be produced from a wide variety of sources. One source is from renewables like nutshells and others that are known from the production of activated carbons. Also synthetic sources can be used. Essential is the activation of the carbon surface. One advantage of these EDLCs is their high cycle life with more than one million cycles.

In a fuel cell the reactive components hydrogen and oxygen are separated from each other by a gas diffusion layer (GDL). The components diffuse through a

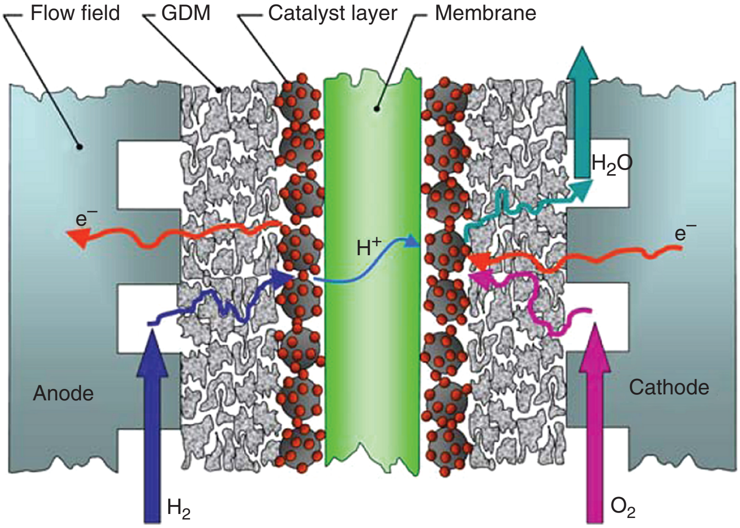
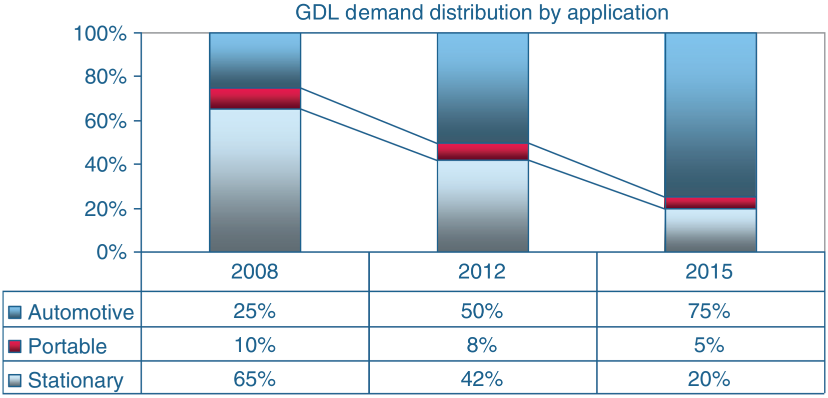


Figure 1.26 Fuel cell schematics.



	2008	2012	2015
▨ Automotive	25%	50%	75%
■ Portable	10%	8%	5%
☐ Stationary	65%	42%	20%

Figure 1.27 Fuel cell demand distribution by application.

gas penetrable layer formed by carbon materials until they reach the catalyst (Figure 1.26). The application of fuel cells is expected to concentrate on automotives and less on portable and stationary systems (Figure 1.27). Main industrial players in the field of GDL are located in Germany and Japan (Figure 1.28).

Redox flow battery systems are suitable for stationary energy storage systems. As carbon components they contain graphite felt and a bipolar plate out of graphite. Although this storage system is not yet widely installed, the forecast is promising (Figure 1.29). Yet the production capacities are small (Figure 1.30).

Graphite is an interesting candidate for systems for the storage of thermal energy. The thermal conductivity of fine-dispersed graphite can be used in cooling and heating systems, for example, for the room conditioning of buildings

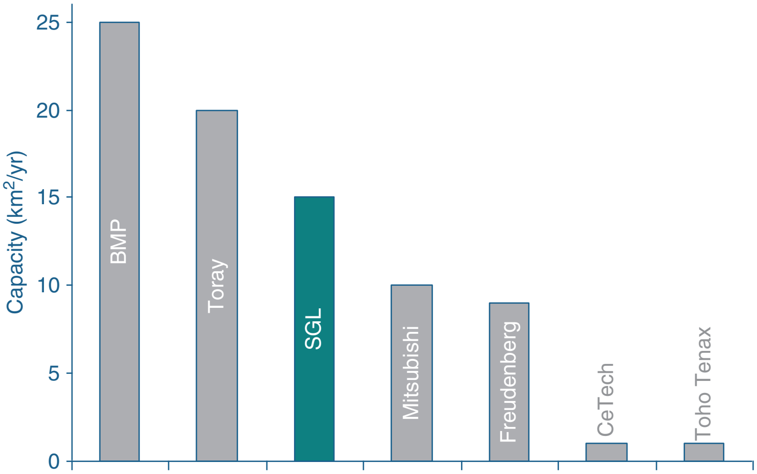


Figure 1.28 Gas diffusion layer production capacity.

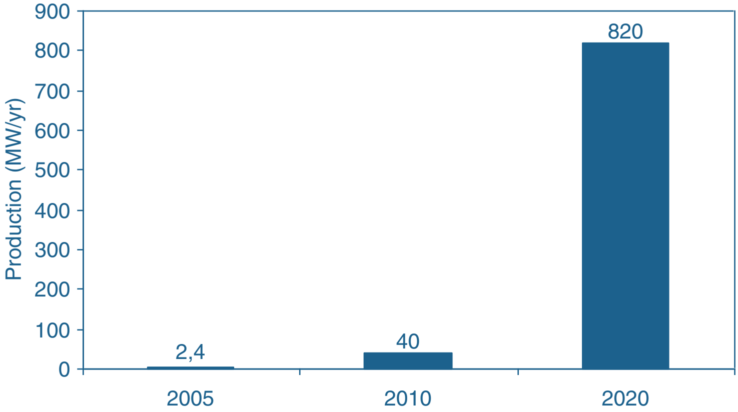


Figure 1.29 Redox flow battery production. Source: EscoVale Study – FlowBatteries, Dec. 2006.

or the storage of thermal energy. These systems are developed and tested currently. Latent heat storage systems have been commercially installed in air-conditioning system for trucks.

1.4 Future Application of Carbon Materials

Tremendous future perspectives for carbon were forecasted with the discovery of nanoscaled new allotropes of carbon. Fullerenes were discovered in 1985 and became immediately a main research area in the field of carbon. The first Nobel Price was conferred in 1996 to H.W. Kroton, R.F. Curl, and R.E. Smalley for the discovery of fullerenes. The number of discussed potential applications reached from anti-abrasive application to drug carrier in living organisms.

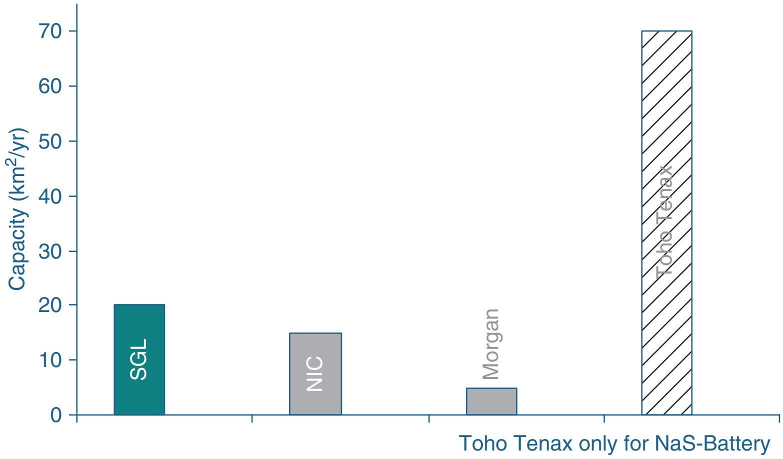


Figure 1.30 Production capacities for redox flow batteries.

None of the discussed applications were realized. The discovery of single-wall nanotubes (SWCNT) and multiwall nanotubes (MWCNT) created new ideas in regard to their outstanding mechanical and electrical properties (Figure 1.31). SWCNT are still of academic interest only. MWCNT are industrialized in a few hundred ton scale and seem to find applications in functional polymers. The second Nobel Prize on carbon was granted to Konstantin Novoselov and

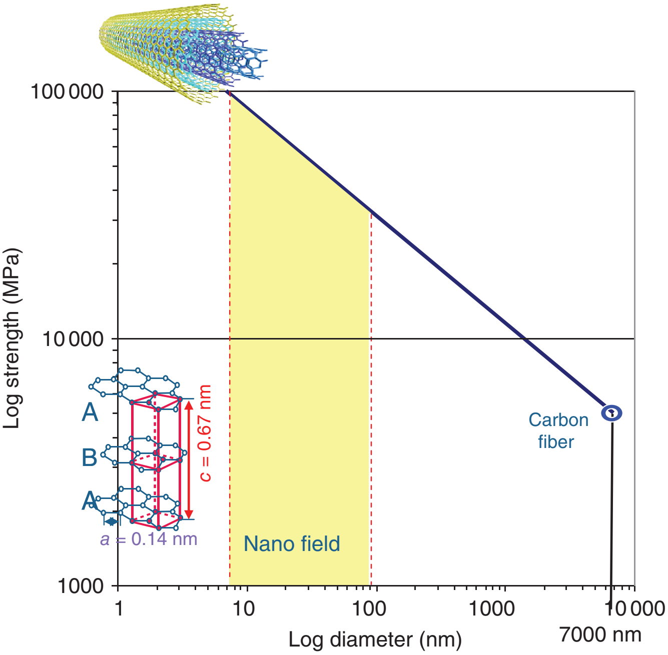


Figure 1.31 Mechanical strength from carbon fibers to nanotubes.

André Geim for their work on graphene and its electrical properties. A very promising application of revolutionary impact in microelectronics may come from graphene sheets. Template-grown graphenes are considered as very promising in this regard. The work of W. de Heer in this field was granted in 2011 by the SGL Carbon Group with the new established Utz-Hellmuth Felcht Award.

1.5 Conclusion

The demand for traditional carbon and graphite products will be further growing and stay the basic business for the carbon and graphite industry. Despite the age of these products, there is still room for scientific research and innovation. The economic growth drives the resources of raw material to the edge. This is also the case for the production of carbon and graphite. Natural graphite is on the European list of short raw materials. Good quality anode coke went short with the strong growth in the production of aluminum. Crude oil refinery exits in a market with regional overcapacities might shorten the availability of petroleum needle coke in the future. Legislative actions in Europe (REACH) will limit the use of coal-tar pitch and petroleum pitch. The industry would appreciate if academia would turn parts of their recourses back to this field and would work jointly with industry on these issues.

The debate about energy production, efficient use, and last but not least about CO_2 release is impacting the human society globally. Lightweight construction with carbon fibers is a market with a huge potential to grow. Also in this field the close interaction between science and industry is necessary to solve open questions in materials science, production, and the development of alternative precursor and matrix systems.

Energy storage for e-mobility and stationary systems needs further research and innovation. The area of nanoforms of the element carbon remains at the very beginning of commercialization.