WP5 TASK 5.1

Solid carbon products and markets

ABSTRACT

A feasible way to utilize CO2 might be to reduce (convert) it to valuable carbon products. One novel way to produce carbon products is the molten salt electrolysis. It utilizes high temperature and electricity to efficiently produce nanocarbon structures. In this part, the solid carbon product and markets were evaluated. First, a literature study of the existing solid carbon products like carbon fibers, carbon nanotubes and carbon nano-onions were studied. The graphite is largest carbon product, but for the nanostructures, carbon nanofibers are currently dominating the market and are increasingly growing. Secondly, a feasibility study of the carbon nanostructures production was conducted. The production cost of the carbon nanotubes was found to be less than 2 €/kg. By this price the production of it is feasible and the development of the technology should be continued. A carbon product from 5th Innovation Ltd was tested for being utilized as electrodes of lithium carbonated based molten salt electrolysis at Tampere University. Their biobased solid carbon was stable as cathode and may substitute typical Nickel cathode, but the oxidative conditions at anode corroded the carbon in tested 30 minutes run.

MOTIVATION

Solid carbon products can become a valuable and feasible way to utilizateCO2 in the existing market products to replace their fossil and mineral peers. Thus, it is important to study the existing markets and the prices of the products. The particular focus of the study was on the nanostructures that are produced by molten salt electrolysis as it is found to be a potential production technology [1]. Different allotropies were studied [2].

APPROACH

Pure carbon products are required in many applications e.g., as carbon black (color, reinforcing filler material). Nanotubes are potential high-value products which can be used in electrodes of batteries and fuel cells and as a semiconductor in electronic components.

Different applications set different requirements for carbon properties e.g. by means of morphology and purity. That is why also the price of carbon products varies significantly affecting the profitability of molten carbonate electrolysis-based carbon production.

The work consisted of three different tasks, and the literature review was made on existing solid carbon product market using scientific and internet sources. The first part studied the prices and markets for selected carbon allotropes [3]. The second part studied the solid carbon products of molten salt electrolysis, and a literature review and a case study of feasibility were conducted [4]. The third part was made in collaboration with 5th Innovation company to study the stability of their bio-based solid carbon as the electrodes of molten salt electrolysis [5]. In addition, during the project, the utilization of the products was evaluated in the end of the project.

RESULTS

The market development of Carbon nanotubes (CNT), Graphene, Grafite and Carbon nanofibers were studied. The market estimates are presented in Figure 1. The largest market is for graphite, and it is also estimated to grow faster than CNFs. CNFs are reaching some billion dollars market by 2030. The markets of graphene are remaining low, rising to approximately one billion dollars annually by 2030.

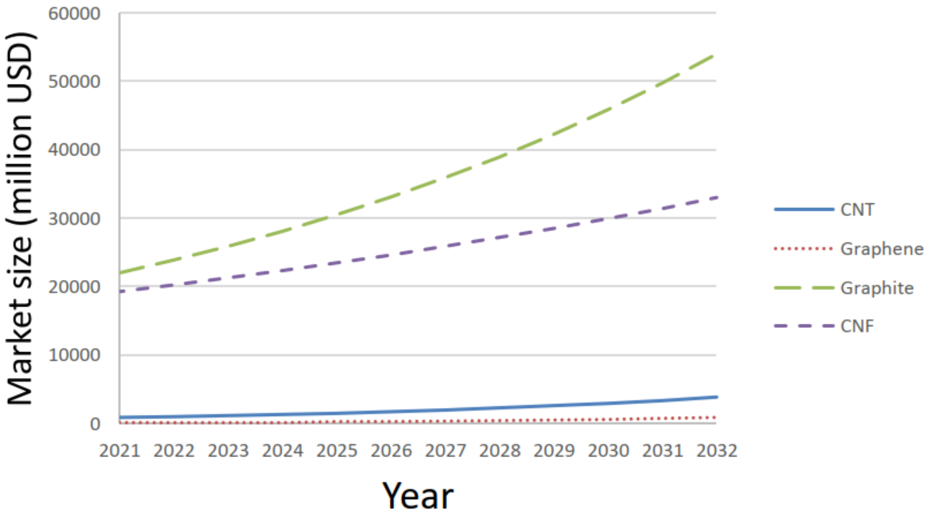

Figure 1. The estimated markets of Carbon nanotubes (CNT), Graphene, Graphite, and Carbon nanofibers. [3]

The price estimates of carbon types of graphite, Single wall carbon nanotubes (SWCNT), Double wall carbon nanotubes (DWCNT), multi wall carbon nanotubes (MWCNT), carbon nano-onions (CNO), carbon nanofibers (CNF), and graphene are presented in Table 1. The prices are significantly affected by the quality, purity, and production method of the material. Pure graphene is the most expensive, and high-quality nanostructures are of high value in addition. If pure nanostructures could be produced by molten salt electrolysis, its production would become feasible. However, the market analysis also revealed that the markets of the most expensive products is rather limited. Mass produced products are always relatively mildly priced. Based on the test runs, the obtained product of nano-onions [6] was in the optimal range for quality and prices.

Table 1. Reported prices of different carbon types [3]

Carbon type	Price per mass	Reference
Graphite	600–2,750€/t	[7, 8]
SWCNT	28–2,800€/g	[5, 11]
DWCNT	14€/g	[5, 11]
MWCNT	0.085–140€/g	[5, 11, 27]
CNO (fullerenes)	129–373€/g	[17]
CNF	2,350–8,900€/kg	[10, 11]
Graphene	70–237,000€/kg	[21 ,11]

An industrial case was studied in a techno-economic study. The applied parameters are presented in the Table 2 and 3. The results of the cost estimation for a CNT production plant having a 0.7 kg/hour production capacity were estimated. The estimated production cost was found to be 1.35 €/kg. However, this estimate is based on small scale production, and might thus be quite optimistic by nature, and therefore the error marginal of the results is large. The result can be considered only as an indicative value. The financial estimate would be fully reliable when demonstrated on a real operating plant in an industrial scale.

Table 2. The values applied in the economic analysis.

Parameter	Value	Unit
Inflation	1.5	% [24]
CO_2	80	€/t [23]
Reference year	2022	
Operational hours	8000	h/a
Discounting rate	10	%
Operational years	30	a
Electricity cost	70	€/MWh [20]
CNT price	100	€/kg [31]
CNT production rate	0.7155	kg/h [7]
Initial investment	7813.124	€ [32]

Table 3. The cost estimates of large-scale molten salt electrolysis process.

Parameter	Cost	Unit	Reference
Electricity	915.95	€/t	[7]
Labour	140.90	€/t	[7]
Capital expenses	230.75	€/t	[7]
Maintenance	61.08	€/t	[27, p.13]
Total	1348.76	€/t	

In the tests of the solid carbon electrode material produced by 5th Innovation a molten salt electrolysis process developed at Tampere University was applied as Cathode [5]. A photo of the equipment is presented in Figure 2 below.

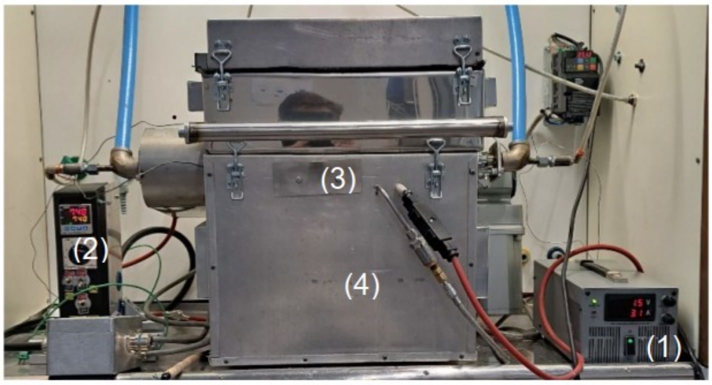

Figure 2. The molten salt electrolysis equipment (1) power source, (2) temperature controller, (3) opening for the electrode holders, and (4) the oven. [5]

In the tests, nominal result was obtained by stable electrode materials studied earlier in HYGCEL project Nickel for cathode and Tin dioxide for anode. The basic electrodes are presented in Figure 3.

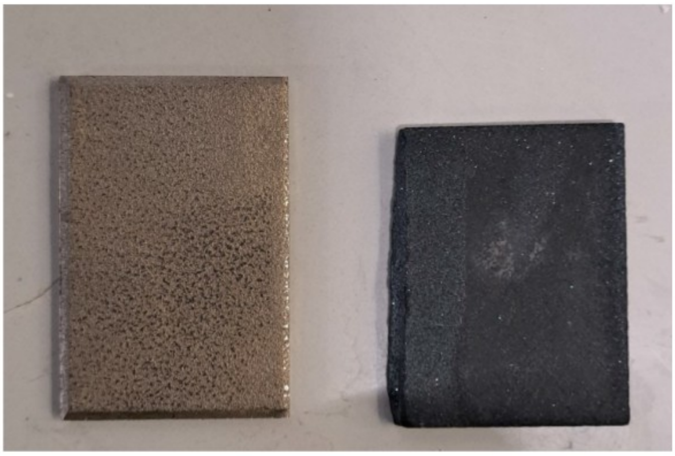

Figure 3. the electrodes applied in the nominal case, left Nickel for cathode and right Tin dioxide for anode. [5]

A stable combination for the tested carbon electrode was made for the cathode. The tested electrodes are shown in Figure 4.

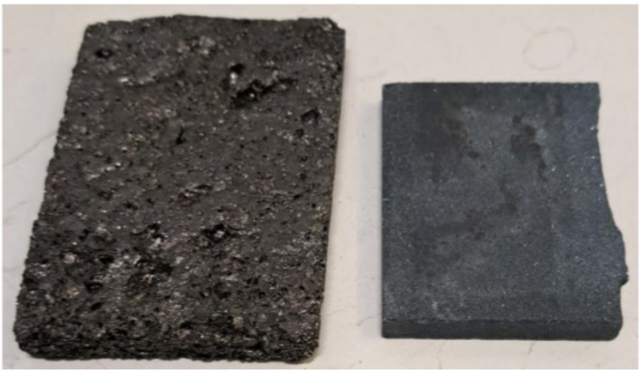

Figure 4. Successfully tested electrodes, left biobased solid carbon cathode and right the Tin dioxide anode. [5]

The carbon was produced on the surface of the cathode. The used electrodes are presented in Figure 5.

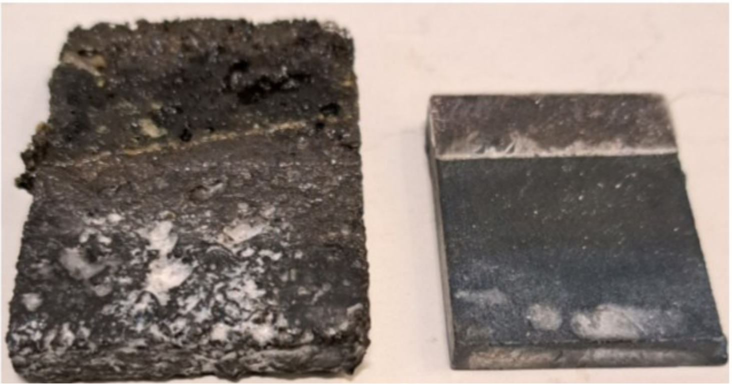

Figure 5. Used biobased cathode on left and anode on right. White contamination on the cathode is lithium salt. [5]

A standard results of carbon nano-onion was found from the washed cathode. A SEM figure is presented in Figure 6.

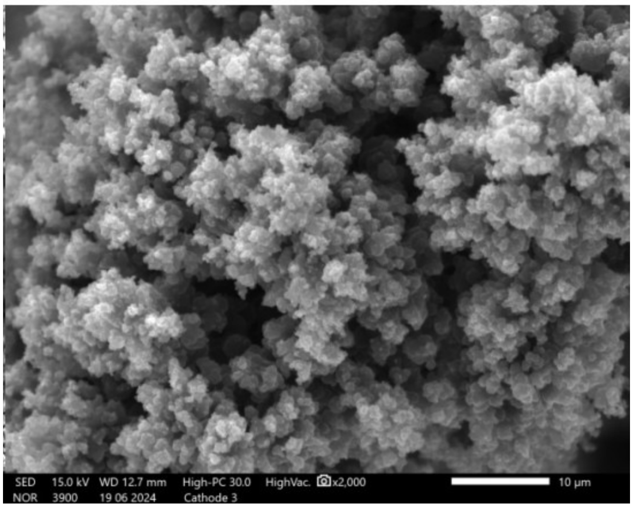

Figure 6. Homogeneous and pure nano-onion sample obtained on the bio-based carbon cathode. Photo by Jussi Laurila. [5]

In the analysis of the produced carbon nano-onions at Tampere University [6] it was analyzed that the specific surface area of the carbon is relatively low 7 m2/g. This limits the utilization of the carbon, and for example, applications of superconductors or filters are not feasible. The application as raw materials of electrodes for batteries and electrolysis are further studied in further coming projects.

APPLICATIONS/IMPACT

The solid carbon products markets are growing fast, and feasible products that are of high price are available. The production is an area of high interest.

The bio-based solid carbon of 5th Innovation is stable in molten salt electrolysis at cathode.

In the analysis of the produced carbon nano-onions at Tampere University [6] it was analyzed that the specific surface area of the carbon is relatively low 7 m2/g. This limits the utilization of the carbon. Applications of superconductors or filters are not feasible. The application as raw materials of electrodes for batteries and electrolysis are further studied in further coming projects.

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