

LAPPEENRANTA-LAHTI UNIVERSITY OF TECHNOLOGY LUT
LUT School of Energy Systems
Degree Programme in Electrical Engineering

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High temperature electrolysis of carbon dioxide

Examiners: Jero Ahola
Antti Kosonen

ABSTRACT

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As the amount of atmospheric carbon dioxide increases, new climate agreements are being signed limiting greenhouse gas emissions. However, limiting these emissions alone is not enough to maintain the average surface temperature below the agreed levels. This means in addition to transiting to renewable energy sources, technologies that reduce the atmospheric carbon dioxide concentration are being developed. One such technology is direct air capture, which captures carbon dioxide directly from air. This captured carbon dioxide contains important elemental building blocks for different technological systems, meaning that otherwise unwanted carbon dioxide can be utilized.

One way to utilize carbon dioxide is by electrochemically reducing it to carbon/carbon monoxide and oxygen by using an electrolysis process carried out in high-temperature molten salts. The most commonly the electrolysis process is carried out in lithium carbonate, that is heated to 750–950°C. The electrolysis process produces carbon monoxide at temperatures over 900°C from where the end product gradually shifts to carbon structures. The structure of the forming carbon product can be modified by altering different process conditions.

The goal of this thesis is to carry out a literature-review on high-temperature carbon dioxide electrolysis process, depict how the process works and what kind of known challenges has been encountered. The thesis also considers different possible end products, how they can be used in different technologies and compares the production costs of different end products using electrolysis process to the production costs of currently used methods. The thesis also ponders what role this electrolysis technology will have in the future energy systems and how the technology will develop in the near future.

Tiivistelmä

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Hiilidioksidin korkealämpöinen elektrolyysi

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Ilmakehässä olevan hiilidioksidin määrän kasvaessa useita, ilmastopimuksia päästöjen rajoittamiseksi on solmittu. Päästörajoitukset eivät kuitenkaan itsessään pysty enää pitämään maan lämpötilan nousua sovitussa rajoissa. Tämän takia uusiutuvan energian tuotannon lisäämisen lisäksi, erinäisiä hiilidioksidin poistoteknologioita on kehitetty. Yksi tämänlainen teknologia on *direct air capture*, joka poistaa hiilidioksidia suoraan ilmasta. Tämä kaapattu hiilidioksidi sisältää tärkeitä alkuaineita, joita voidaan käyttää rakennuspalikoina erilaisille teknologisille systeemeille. Tämä tarkoittaa, että muutoin lähes hyödytöntä hiilidioksidia voitaisiin muokata hyödyllisiksi tuotteiksi.

Yksi tapa muokata hiilidioksidia on sen hajottaminen hiileksi/hiilimonoksidiksi ja hapeksi käyttämällä korkealämpöisessä sulasuolassa tapahtuvaa elektrolyysiä. Tavallisimmin elektrolyysireaktio toteutetaan elektrolyytinä toimivassa litiumkarbonaattiyhdisteessä, joka on lämmitetty 750–950°C. Elektrolyysireaktio tuottaa puhdasta hiilimonoksidia yli 900°C lämpötilassa, josta lopputuote hiljalleen muuttuu hiileksi, ja 800°C lämpötilassa tuote on kokonaan hiiltä. Hiilituotteen rakennetta voidaan muokata muuntelemalla prosessiolosuhteita.

Tämän työn tarkoituksena on tarjota kirjallisuuskatsaus korkealämpöisestä hiilidioksidin elektrolyysiteknologiasta, kuvata kuinka prosessi toimii ja mitä tunnettuja ongelmia prosessissa on esiintynyt. Työ myös käsittelee eri lopputuotteiden käyttökohteita, sekä vertailee tuotteiden tuotantokustannuksia nykyisillä tuotantomenetelmillä elektrolyysiprosessin vastaaviin tuotantokustannuksiin. Työ myös pohtii teknologian tulevaisuudennäkymiä, sekä sen roolia tulevaisuuden energiasysteemissä.

PREFACE

This thesis was completed in the Laboratory of Digital Systems and Control Engineering in Lappeenranta-Lahti University of Technology LUT. I would like to thank my examiners Jero Ahola and Antti Kosonen for introducing me this interesting topic and giving help and feedback during the process of writing this thesis.

I would also like to thank my family for always supporting me through my education and my friends for providing much needed breaks within all the school and work.

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SYMBOLS AND ABBREVIATIONS

Roman letters

<i>A</i>	Area
<i>c_p</i>	Specific heat capacity
<i>d</i>	Diameter
<i>E</i>	Energy
<i>F</i>	Faraday constant
<i>G</i>	Gibbs free energy
<i>H</i>	Enthalpy
<i>I</i>	Current
<i>j</i>	Current density
<i>k</i>	Thermal conductivity
<i>m</i>	Mass
<i>M</i>	Molar mass
<i>n</i>	Number of electrons
<i>P</i>	Power
<i>Q</i>	Electric charge
<i>Q</i>	Heat transferred
<i>S</i>	Entropy
<i>T</i>	Temperature
<i>U</i>	Voltage
<i>v</i>	Generation rate

Greek letters

η	Efficiency
--------	------------

Subscripts

an	Anode
cell	Cell
Cold	Cold
ct	Cathode
ext	External
heat	Heat
hot	Hot
kiln	Kiln
rev	Reversible
th	Thermal
tn	Thermoneutral
tot	Total
U	Voltage
w	Wall

Acronyms

CNF	Carbon nanofiber
CNT	Carbon nanotube
CVD	Chemical vapor deposition
DAC	Direct air capture
HP	High performance
MWCNT	Multi walled carbon nanotubes
NDC	Nationally determined contributions
NET	Negative carbon dioxide emission technology
PAN	Polyacrylonitrile
PV	Photo voltaic
STEP	Solar thermal electrochemical process
SWCNT	Single walled carbon nanotubes

1 INTRODUCTION

Carbon dioxide (CO₂) belongs in a group of gases that absorb and emit infrared radiation. This type of gases is also known as greenhouse gases which are vital for the climate of Earth: without the natural greenhouse effect, the average temperature of Earth would be near -18°C instead of the current about 14.9°C. The amount of greenhouse gases in the atmosphere of Earth have fluctuated naturally over time causing the average surface temperature of Earth to vary. In general, higher the greenhouse gas concentration in the atmosphere, higher the average surface temperature. (NASA, 1998).

The global average surface temperature has been steadily increasing over the past couple of centuries. Fig. 1.1 presents the global temperature change from pre-industrial levels during 1880–2016.

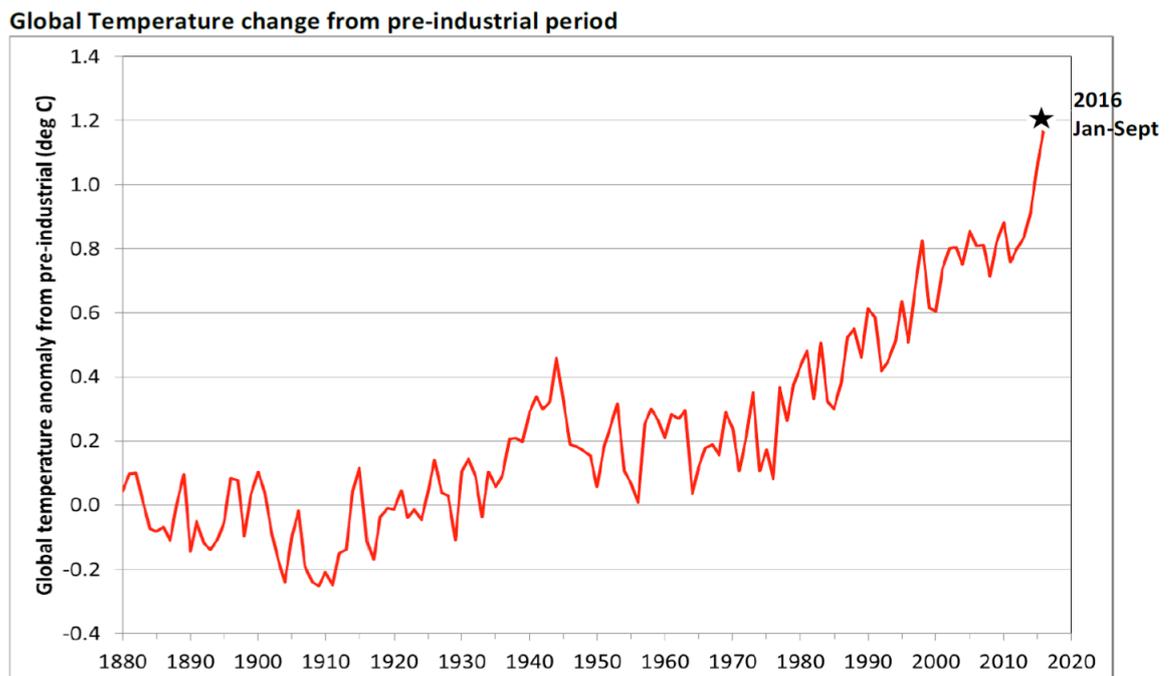


Figure 1.1. Global average surface temperature from 1880 to 2020. (WMO, 2016)

The temperature rise seen in Fig. 1.1 can be mostly explained with increasing levels of greenhouse gases and is termed global warming which is an aspect of the constantly ongoing climate change. Out of the greenhouse gases, the increase of atmospheric CO₂ is the most noticeable; CO₂ levels reached 400 ppm in 2013 for the first time in the past 800 000 years, and the trend is still upwards. It is estimated that human activities, since the start of the

industrial revolution (1750), have caused a substantial increase of 45% in concentration of the atmospheric CO₂. This increase is primarily due to the burning of fossil fuels which release CO₂ to the atmosphere in significant amounts, and the trend continues as long as fossil fuels are being burned. (Climate, 2018). Fig. 1.2 presents the atmospheric CO₂ concentrations since 1700 – values before 1958 are evidence from ice cores and the values after are daily measures taken in Hawaii.

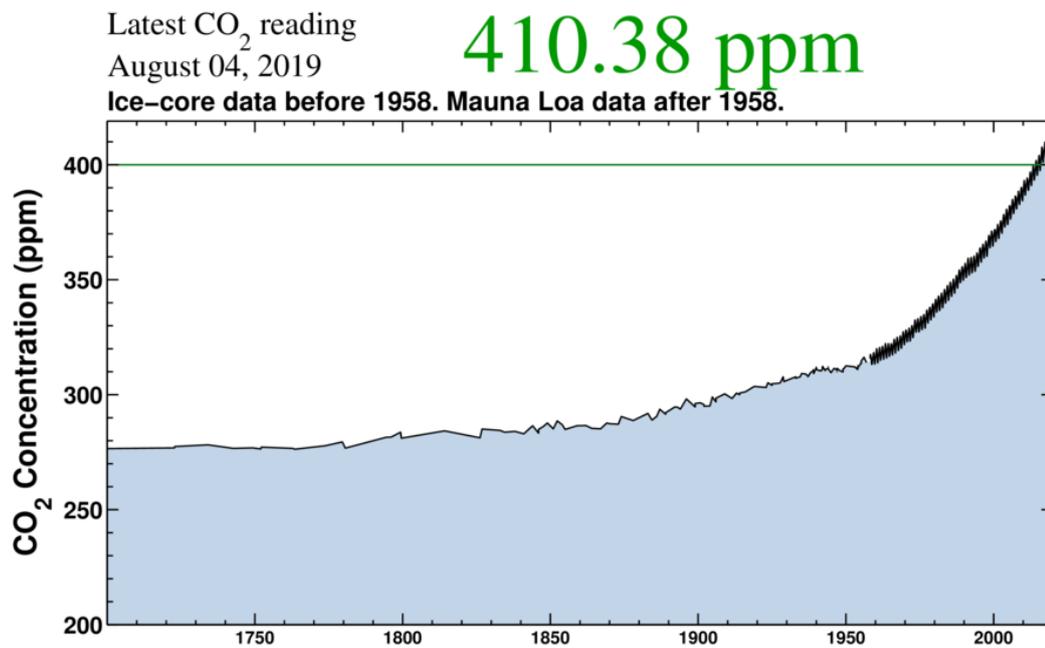


Figure 1.2. Keeling Curve, atmospheric CO₂ concentrations since 1700. (Scripps, 2019)

By comparing Figs 1.1 and 1.2, we can see a noticeable trend of increase in both CO₂ concentration and average global temperature change since 1950s, providing further confirmation of the correlation between the two.

CO₂ emissions account for the most of all the greenhouse gas emissions caused by human activities. For example, in 2010, the CO₂ emissions totaled to 76% of all greenhouse gas emissions of the world, as can be seen in Fig. 1.3.

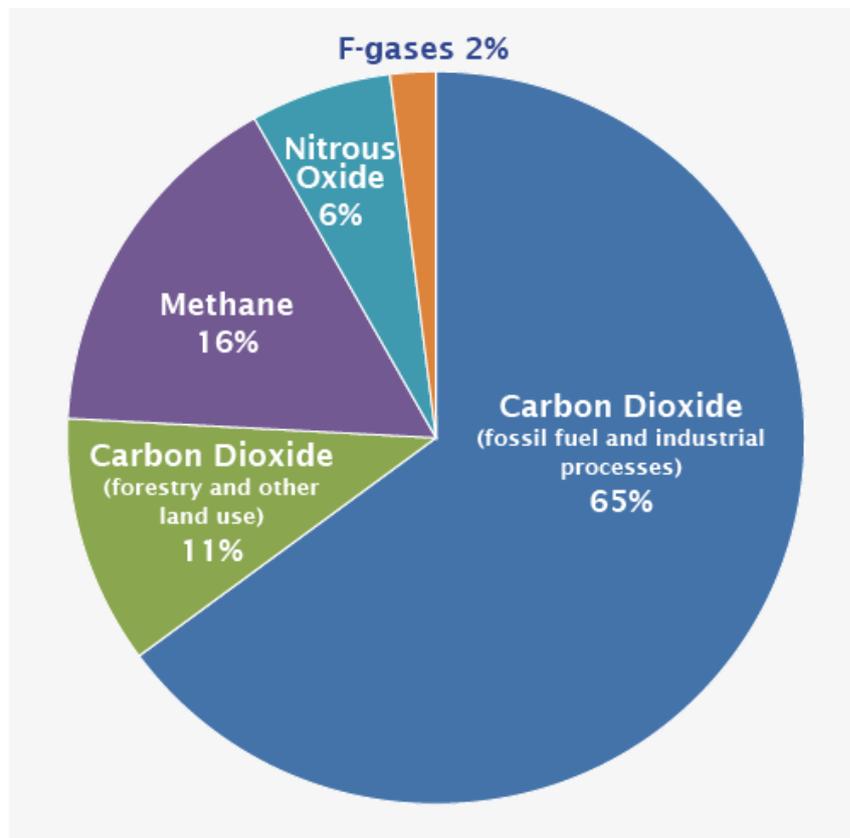


Figure 1.3. Global greenhouse gas emissions in 2010 categorized into different gas types. (IPCC, 2014)

If the global CO₂ emissions were decreased, the temperature increase could be stopped. This is because the existing atmospheric CO₂ would be removed from the atmosphere by so called carbon sinks, and if the carbon sink removal capacity is greater than the total global CO₂ emissions, the CO₂ concentration would begin to decrease. The primary natural carbon sinks are plants, soil and the ocean and currently, on average, they absorb over half of the CO₂ emissions caused by human activities (Sitch et al., 2015).

To combat the increasing atmospheric CO₂ concentration and global average surface temperature many countries have agreed to decrease their greenhouse gas emissions. In 2016, 195 countries signed the Paris Agreement where signing governments agreed to the goal of keeping the global average surface temperature increase below 2°C from pre-industrial temperatures. To achieve this goal all member parties of the Paris Agreement agreed to nationally determined contributions (NDC) which determine how this long-term goal is achieved. In case of the European Union this means a 40% decrease in greenhouse gas emissions compared to 1990 by 2030. (Europa, 2016). The target set in the Paris Agreement can be accomplished by substituting fossil energy with renewable energy sources

and it has had great impact in the increase of the usage of renewable energy sources. The share of renewable energy production of the total energy consumption has increased over the past 20 years; especially the amount of wind and solar photovoltaic (PV) energy production capacities have increased exponentially during 2000–2018 and the trend is still upwards. Figs. 1.4 and 1.5 illustrate this exponential trend and show the development history of these two renewable power generation capacities.

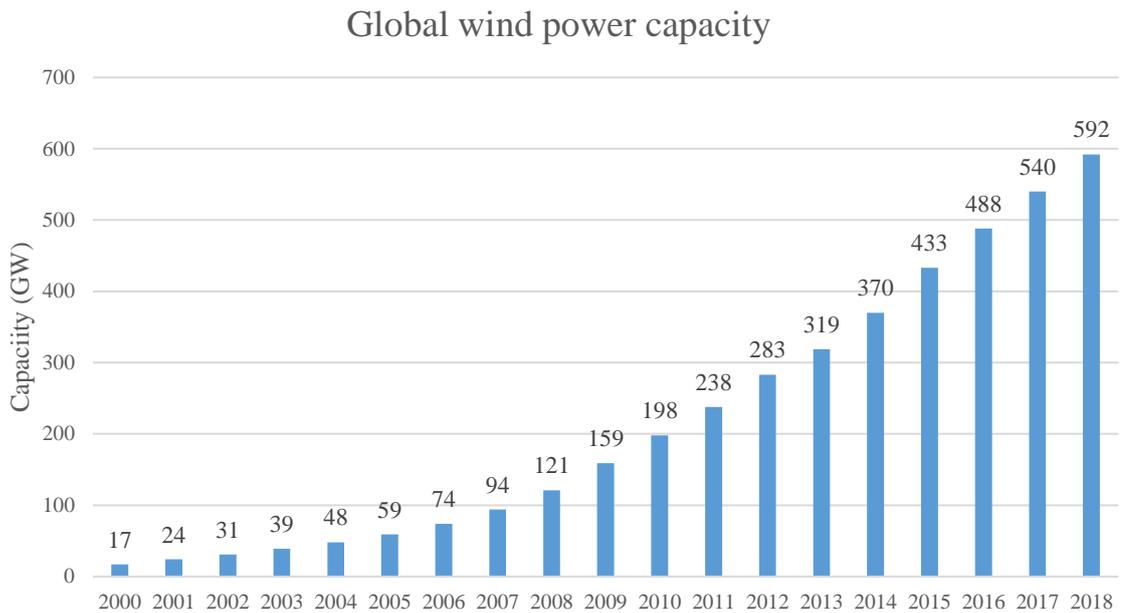


Figure 1.4. Global installed wind power capacity 2000–2018.

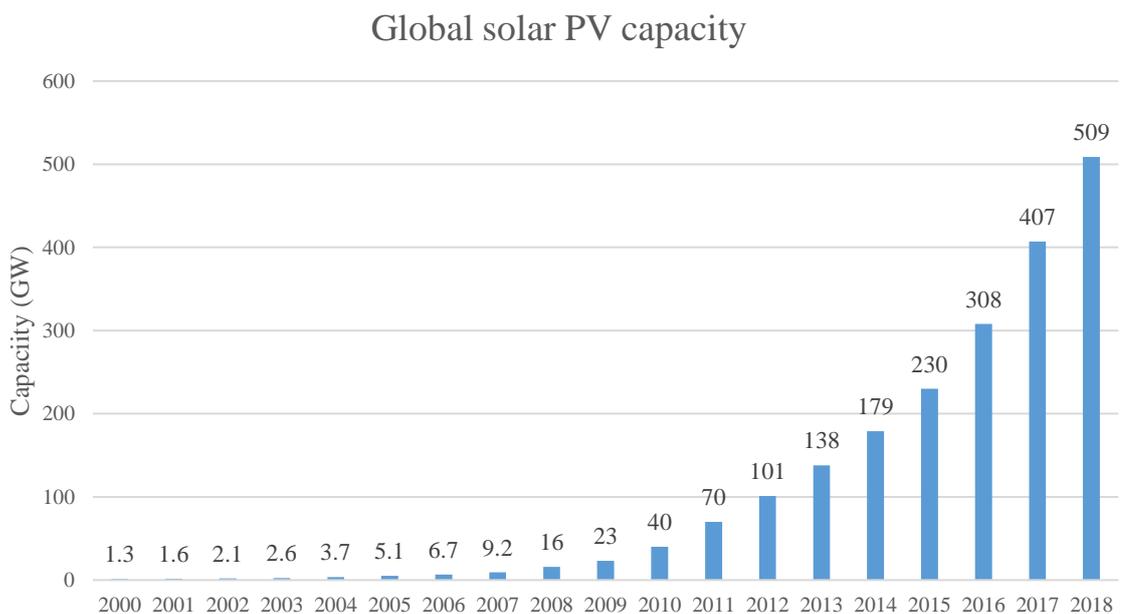


Figure 1.5. Global installed solar PV power capacity 2000–2018.

As can be seen from Figs 1.4 and 1.5, the global solar PV capacity has reached 509 GWp and the global wind capacity has reached 592 GWp, and the total solar PV capacity is expected to increase past total wind capacity in near future. The exponential increase in these two generation capacities has created challenges caused by the great variance in electricity production due to the fact that the electricity generation in these two are highly dependable on the generation conditions, such as the amount of irradiation and wind. This brings up a need for new energy storage methods and methods to even out the electricity generation and ensure flexibility of the grid. In addition, because the production of renewable energy with traditional solar PV and wind power is rather unreliable and often occurring in remote locations, finding a valid method to transport and store renewable energy is desirable.

Even though the trend of adapting renewable energy sources has been good worldwide, the shift to a 100% renewable energy world is not easy nor fast. Vast past and present greenhouse gas emissions have caused that it is no longer possible to keep within the temperature rise range of the 1.5–2°C agreed upon in the Paris Agreement. This means that technologies which remove CO₂ from the atmosphere, also known as negative carbon dioxide emission technologies (NETs), are required to limit the temperature rise within the target range. (Breyer et al., 2019). Different kinds of NETs to assist the decrease of the atmospheric CO₂ concentration are constantly being developed, and one such technology is an already existing direct air capture (DAC). DAC is a carbon capture method that separates CO₂ directly from air, decreasing the atmospheric CO₂ concentration by acting as a manmade carbon sink. These kinds of manmade carbon sinks could aid the natural carbon sinks by increasing the total amount of CO₂ extracted from the atmosphere, maybe even increasing the net amount to the point that more CO₂ is bound from the atmosphere than it is being emitted. This could cause the CO₂ concentration in the atmosphere to decrease which in turn would cause the end to the global warming caused by human activities. CO₂ contains oxygen and carbon, which are important building blocks for different technological applications, meaning that the captured CO₂ can be further utilized as fuels or other materials, such as highly valuable carbon nanofibers (CNFs). In addition, CO₂ utilization provides a good solution for the considerable seasonal differences in weather conditions and time of day fluctuation of the wind and solar PV power generation, for the processes can be run during at times of surplus power supply and the resulting end products can be used as energy storages that can be

utilized to ensure the availability of energy during times of lower renewable energy generation, such as night and winter time.

Carbon dioxide electrolysis could provide a solution to the climate change and a great solution to utilizing CO₂ by transforming the unwanted captured CO₂ into more usable chemical structures. The principle is similar to water electrolysis, where hydrogen is separated from water via electrochemical reduction of water, but in the case of carbon dioxide electrolysis elemental carbon or carbon monoxide (CO) is separated from CO₂. Resulting CO could be then used as a fuel in a gas turbine to generate electricity, for example, or it could be further processed into methanol (Kaplan et al., 2014). In turn, the resulting elemental carbon could be used to form complex carbon nanostructures, for which applications range from Li-ion batteries and catalysts to lightweight, strong building materials. The formation of nanostructures can be controlled during electrolysis by varying the process conditions (Ren et al., 2015).

1.1 Objective of the thesis

The objective of this thesis is to describe the state-of-the-art carbon dioxide electrolysis and how it differs from the more traditional water electrolysis and the paper is mainly carried out as a literature review. This thesis also presents different end products obtained from carbon dioxide electrolysis and brings attention to the possible methods of utilization of the said different end products. The electrochemistry and the thermodynamics behind the electrolysis process are also provided, existing carbon dioxide electrolysis technologies are discussed, the future of carbon dioxide electrolysis is considered and the ways to overcome recognized challenges faced in CO₂ electrolysis are discussed.

1.2 Outline of the thesis

Rest of the thesis is structured as follows:

1. the fundamentals and the basic theory of electrolysis is introduced, differences between more traditional water electrolysis compared to CO₂ electrolysis are discussed and basic chemical reactions occurring within CO₂ electrolysis are presented.

2. The associated electrochemistry alongside with thermodynamics are described and key performance indicators of the electrolysis process are discussed.
3. Different challenges faced in CO₂ electrolysis are presented and methods to overcome these challenges are discussed.
4. Materials for anode, cathode and electrolysis container are discussed and different electrolyte options are compared, their advantages discussed, and the best alternatives are chosen.
5. Different carbon products are presented, their applications are discussed, their production methodologies are compared with the possibility of CO₂ production and the production cost differences between different production technologies are analyzed.
6. Existing CO₂ electrolysis technologies are considered, previous findings are presented, and the future of the technology is discussed.
7. The CO₂ electrolysis technology is discussed and its role in the future is considered.
8. The topics discussed in this thesis are summarized.

2 CARBON DIOXIDE ELECTROLYSIS

Electrolysis is an old technology: it was invented and first performed in 1800 by William Nicholson and Anthony Carlisle. It took 30 more years for the laws of electrolysis to be discovered by the English scientist Michael Faraday and he found out that the amount of electricity Q has a direct relationship to the mass m of the substance involved in the electrolysis process. (Millet & Grigoriev, 2013). The basic principle of electrolysis process is passing direct current between two electrodes that are immersed in some kind of an electrolyte which causes the conversion of a target product into a more chemically reduced chemical species.

The first electrolysis test was conducted on water causing following water splitting reaction:



and electrochemical reduction of water into hydrogen and oxygen still remains the dominating form of electrolysis. Electrolysis is used as an emission-free way to produce hydrogen and it is used together with steam reforming to produce hydrogen on a large-scale (Bessarabov & Millet, 2018). Fig. 2.1. presents the basic operating principle of an alkaline type water electrolysis cell, which is the most common, developed and mature water electrolysis technology available on the market.

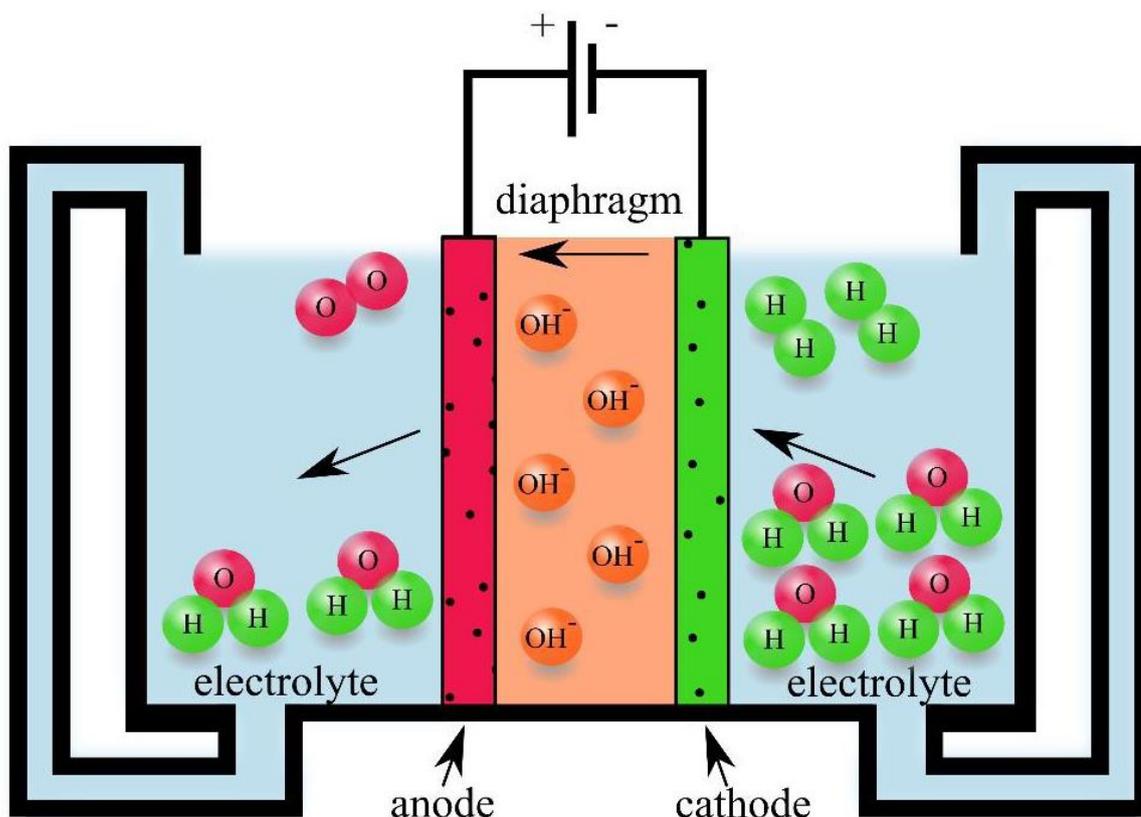


Figure 2.1. Basic operating principle of an alkaline type water electrolysis cell where hydrogen is formed on the cathode and oxygen on the anode. (Koponen, 2015).

However, different types of electrochemical reductions already exist, and new technologies are constantly being developed. One such emerging technology is carbon dioxide electrolysis, where CO_2 is electrochemically broken down into more reduced chemical compounds using electricity as an energy source. The history of electrochemical reduction of CO_2 can be dated to start in the nineteenth century, when CO_2 was first reduced to an aqueous solution, formic acid, using a zinc cathode (Hu & Suib, 2014). Carbon products of interest in this thesis are elemental carbon and CO , that are formed via electrochemical reduction of CO_2 in molten salts, but more focus is brought to the different elemental carbon products due to their value and various applications. The resulting carbon product depends on process conditions, and the chemical reaction equations for these two different CO_2 electrolysis reduction reactions can be written as



and



(Kaplan et al., 2012) (Douglas & Pint, 2017).

2.1 Process fundamentals

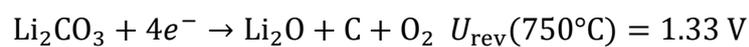
In this chapter thermodynamics and electrochemistry behind CO₂ electrolysis process are described and greater detail is brought into the process itself. Since the process to produce different elemental carbon products seems a more prominent technology due to its valuable end products that have many different applications, this chapter only considers the fundamentals of the production of elemental carbon, instead of the production of CO. These two differ especially in thermodynamics, due to their different process temperatures, but also in electrochemistry. Since Li₂CO₃ is currently the most commonly used process electrolyte, thermodynamic and electrochemical examples are presented on a system that uses Li₂CO₃ as its electrolyte.

Gibbs free energy change ΔG (J), also known as free energy change, is a thermodynamic potential that is used to determine the energy that has to be supplied to the electrodes in form of electrical energy. This free energy change at a certain temperature can be calculated via the enthalpy ΔH (J) and entropy ΔS (J/K) change in the system or by using the reversible cell voltage U_{rev} (V), which is the lowest required thermodynamic voltage for the electrochemical reduction of CO₂ to occur and is known also as the equilibrium cell voltage

$$\Delta G(T) = \Delta H(T) - T\Delta S(T), \quad (2.4)$$

$$\Delta G(T) = nFU_{\text{rev}}, \quad (2.5)$$

where n is the number of electrons transferred in the electrolysis, which is 4 or 2 depending on if CO₂ is converted into solid carbon or CO products respectively and F is the Faraday constant (96 485 C/mol). (Ren et al., 2015). The calculated reversible voltage for the CO₂ four electron reduction reaction at set optimal reaction temperature, which is a little over the melting temperature of Li₂CO₃ (723°C) to ensure that the electrolyte is fully molten, is



In turn, thermoneutral cell voltage U_{tn} (V) represents the voltage required for no heat generation or absorption to exhibit in the electrolysis process and this voltage can be calculated as follows:

$$U_{tn} = \Delta H(nF). \quad (2.6)$$

At 750°C process temperature, the thermoneutral cell voltage is $U_{tn} = 1.43$ V. In the voltage range between the thermoneutral cell voltage and the reversible cell voltage heat is consumed in the electrochemical reduction process, and at voltages above the thermoneutral voltage heat is generated. Voltage range exceeding the thermoneutral voltage is termed overpotential. Fig. 2.2. shows the thermoneutral potential of the electrochemical reduction process at different process temperatures.

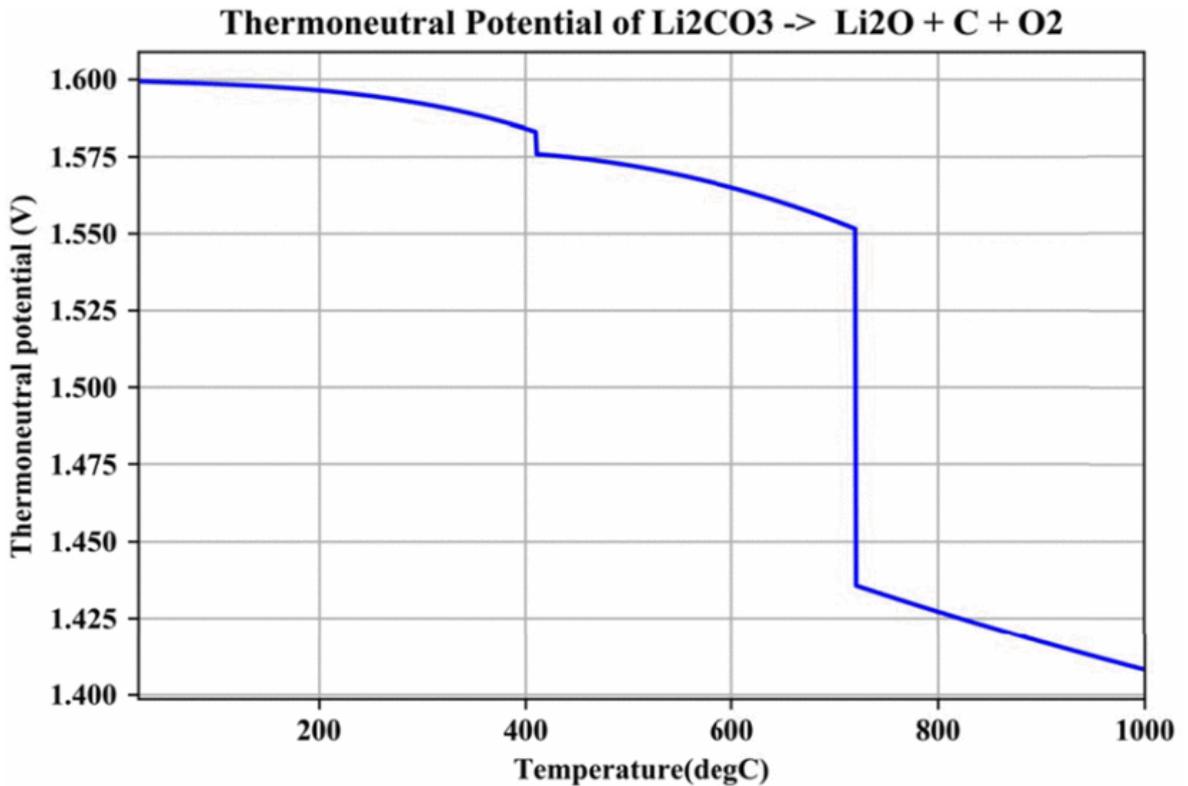


Figure 2.2. Thermoneutral potential of CO₂ electrolysis in lithium carbonate (Peng et al., 2017).

The voltage drop seen in figure above occurs at 723°C, which is the melting temperature of Li₂CO₃. As the electrolysis process temperature increases, both U_{tn} and U_{rev} decreases,

meaning the electrochemical reduction process is more spontaneous in higher temperatures. This could be interpreted so that if heat energy is readily available, electrical energy can be saved by increasing the process temperature. However, because the process temperature is already high, increasing the temperature even further may cost more in energy than just using lower temperature with higher electrolytic potential. Table 2.1 below illustrates the state of electrolysis at different voltages at 750°C process temperature.

Table 2.1. Heat generation and absorption into the system at different process voltages at 750°C process temperature.

Voltage (V)	Electrolysis State
1.33–1.43	Heat is consumed
1.43	No heat generated/consumed
<1.43	Heat is generated

Heat, that is generated into the system by overpotential, can be calculated as follows:

$$P = \Delta U \cdot I = \Delta U \cdot j \cdot A, \quad (2.7)$$

where ΔU (V) is the difference between the reversible cell voltage and the thermoneutral voltage, j (A/m²) is the current density of the process and A (m²) is the effective cell area.

Current density is the amount of electrical charge that flows through a cross section in the electrolyte. In CO₂ electrolysis, typical current density values of existing experimental setups have ranged between 50 and 400 mA/cm². When comparing these to the values of classical H₂O electrolysis, where typical current densities of commercial alkaline electrolyzers range between 100 and 400 mA/cm², a notable similarity can be seen. Increasing the process current density, increases the product generation rate and the Faraday efficiency of the process. However, in CO₂ electrolysis, the higher the current density is, the higher is the anode corrosion (Wu et al., 2017).

CO₂ absorption reaction



is exothermic, meaning the reaction releases heat into the environment. The amount of heat being released is directly subject to the amount of CO_2 being absorbed in the electrolyte, which again depends on the amount of free Li_2O in the electrolyte, and the temperature of the CO_2 being fed into the electrolyte. Ideal Li_2O generation rate during the electrolysis process $v_{\text{Li}_2\text{O}}$ (mol/s) can be calculated as follows:

$$v_{\text{Li}_2\text{O}} = \frac{j \cdot A}{nF}, \quad (2.9)$$

where n is the number of moles of electrons transferred in the reaction which is 4 when producing carbon and 2 when producing CO, and F is the Faraday constant. For every mole of Li_2O generated, a mole of CO_2 can be captured into the system, meaning the CO_2 capture rate v_{CO_2} (mol/s) is

$$v_{\text{CO}_2} = v_{\text{Li}_2\text{O}}. \quad (2.10)$$

The total energy released by the reaction into the electrolyte \dot{E}_{CO_2} (kJ/s) is calculated

$$\dot{E}_{\text{CO}_2} = \frac{j \cdot A}{nF} \cdot \Delta H, \quad (2.11)$$

where ΔH is the specific enthalpy of reaction (2.8), which is presented as a function of temperature in Fig. 2.3.

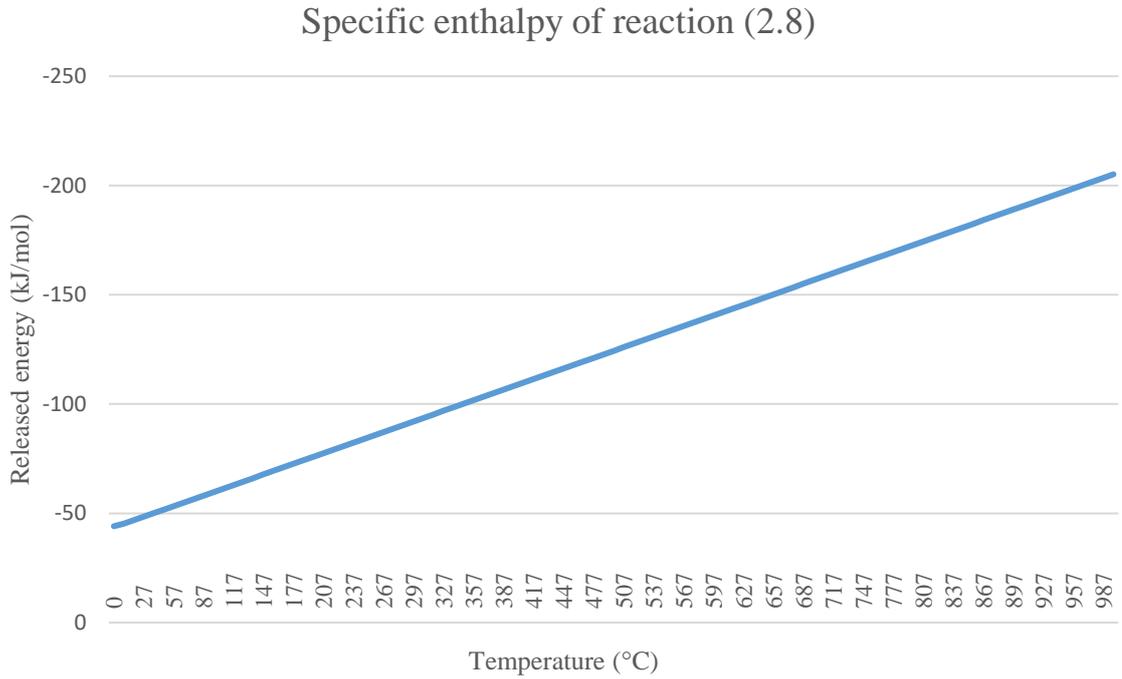


Figure 2.3. Specific enthalpy of reaction (2.8).

At the process temperature, 750°C, the specific enthalpy of the reaction is -158 kJ/mol, meaning the reaction releases 158 kJ/mol of energy (Peng et al., 2017).

2.2 Production performance

There are three different keyways to express the efficiency of CO₂ electrolysis process; voltage efficiency η_U , thermal efficiency η_{th} and Faraday efficiency η_F .

The voltage efficiency describes the voltage losses in the electrolysis system. η_U can be calculated from

$$\eta_U = \frac{U_{an} - U_{ct}}{U_{cell}}, \quad (2.12)$$

where U_{an} (V) is the anode potential, U_{ct} (V) the cathode potential and U_{cell} (V) the cell voltage of the electrolysis process.

The thermal efficiency can be calculated by using known Gibbs free energy and enthalpy change values at process conditions, or by using the thermoneutral voltage and the cell voltage as follows:

$$\eta_{\text{th}} = \frac{\Delta H}{\Delta G + E_{\text{cl}}} = \frac{U_{\text{tn}}}{U_{\text{cell}}}, \quad (2.13)$$

where E_{cl} (J) is the total losses. Faraday efficiency, or also known as current density or Coulombic efficiency, describes the ratio at which the electrolysis process produces the end product compared to theoretical maximum amount of product produced (Ren et al., 2015). Faraday efficiency value of existing systems performing CO_2 electrolysis in Li_2CO_3 ranges between 65–100%, and the efficiency typically increases at higher temperatures. Using the Faraday efficiency together with the assumption that current efficiency remains constant through the electrolytic cell, actual carbon production rate v_c (mol/s) can be calculated as follows:

$$v_c = \eta_F \cdot \frac{j \cdot A}{nF}. \quad (2.14)$$

Further review on energy consumption of CO_2 electrolysis is performed in Chapter 5.3.

3 CHALLENGES IN HIGH TEMPERATURE ELECTROLYSIS

CO₂ electrolysis via molten salts is still a relatively new carbon production method and the amount of research on the technology is still relatively slight. The fact that CO₂ electrolysis is performed in high temperatures with corrosive electrolytes and is not a greatly researched technology brings up several recognized challenges with the process:

- Heating
- Corrosion
- Implementing electrolysis stacks
- Continuous production.

3.1 Heating of electrolysis system

High process temperature is required to keep molten salts used as the process electrolyte in a liquid form. For example, the required process temperature varies between 750°C and 950°C when using Li₂CO₃ as the electrolyte. This high process temperature causes several problems:

- How to heat the system, insulate the system and maintain the temperature at desired levels
- How to ensure sufficient process safety levels
- The electrolyte becomes more corrosive depending on the process temperature causing material problems.

Heating the electrolyte to the desired CO₂ electrolysis levels requires substantial amount of heat energy and the method of heating the system in an energy efficient, safe and economically feasible approach creates challenges for the system implementation. Considering the heat energy needed in the production, the production of carbon structures is simpler than producing CO, since the required process temperature is lower. This means lower production costs due to smaller amount of heat energy required and milder production conditions.

In many existing researches the heating of the electrolysis process was implemented with a solar thermal electrochemical process (STEP) where solar thermal energy is used to heat an electrochemical reduction process. STEP is proven to be a good and sustainable way for the

CO₂ electrolysis process, but the initial investment for the solar thermal system can be relatively high and the process is typically applicable in desert conditions where overcast is minimal. (Licht et al., 2010) (Licht, 2015) (Licht et al., 2016) (Ren et al., 2015)

The heat energy can also be introduced by electrically heating the process container into desired temperature and maintaining the process temperature by keeping the heating value constant. In addition, heat generation within the system can be varied by altering the temperature and the velocity of the CO₂ fed into the system since the reaction described in (2.8) is exothermic and releases 158 kJ/mol of energy when the fed CO₂ is heated to 750°C, and by applying overpotential which can generate heat at rate calculated in (2.7). However, the usage of overpotential to generate heat into the system could damage the electrolysis cells, meaning electrical heating might be a better option. (Peng et al., 2017)

3.2 Corrosion of the process materials

Especially the corrosiveness of molten salts causes significant problems in the electrolysis process; for example, at 950°C Li₂CO₃ with 2 mol of lithium oxide (Li₂O) will dissolve through alumina crucible within two hours. This corrosive characteristic can be decreased by preventing the Li₂O formation by ensuring CO₂ feed into the system. Li₂CO₃ alone is also very corrosive at high temperatures and electrolysis materials have to be chosen carefully. For example, it dissolves through platinum and gold, but it alone does not dissolve thorough the alumina crucible and no mass loss or etching occurs. (Ren et al., 2015)

At lower temperatures the corrosive characteristic of Li₂CO₃ decreases and materials not suitable for electrolysis at 950°C can be used. For example, at 750°C, which is a common CO₂ electrolysis temperature when producing different carbon structures, previously mentioned platinum and gold materials do not exhibit etching or mass loss. (Licht et al., 2015)

Due to the corrosive nature of the electrolyte and high process temperature, the process safety has to be ensured with proper selection of materials. For example, liquid Li₂CO₃ at 750°C will melt through platinum and gold (Kaplan et al., 2013). Material selection will be reviewed in more detail in Chapter 5.

3.3 Other challenges

Li_2O , which is a byproduct from the electrochemical reduction of Li_2CO_3 , is highly corrosive and has much higher melting point than Li_2CO_3 it is reduced from which can be seen from the phase diagram shown in Fig. 3.1.

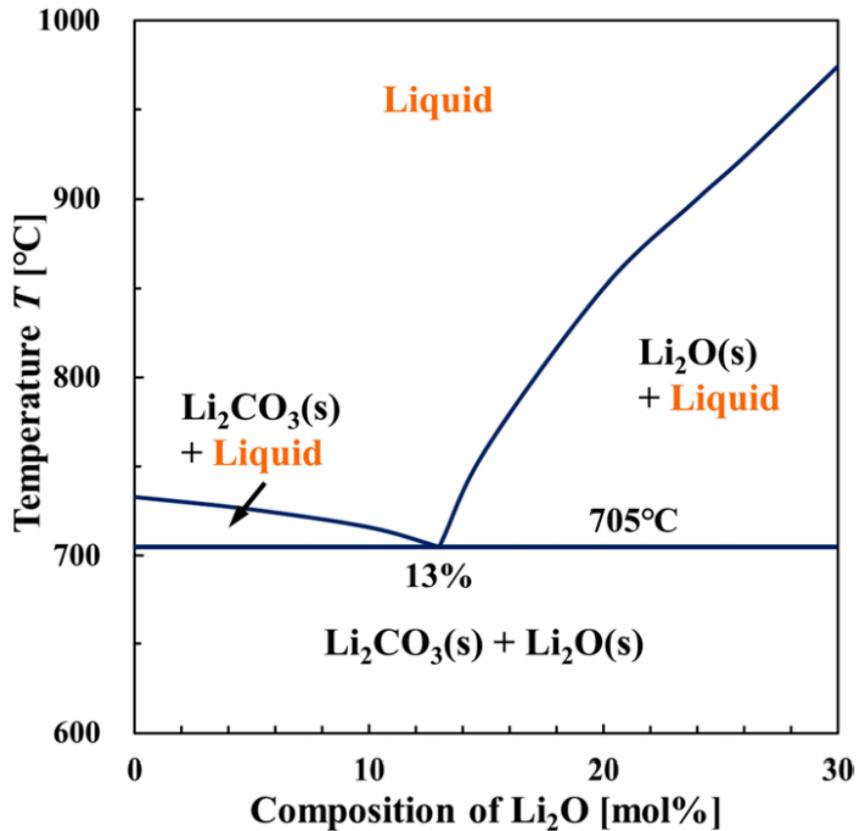


Figure 3.1. Phase diagram of Li_2CO_3 with different amount of Li_2O (Kanai et al., 2019).

However, since the reaction described in (2.8) is exothermic and spontaneous, the formation of Li_2O can be prevented by ensuring sufficient CO_2 feed into the system during the electrolysis process which can be ensured by measuring the amount of CO_2 in the exhaust fumes; if CO_2 is present in the exhaust fumes, Li_2O formation does not occur. . The amount of CO_2 captured into the electrolyte is entirely dependent on the amount Li_2O generated. The best theoretical Li_2O generation rate (mol/s) during the electrolysis process was calculated in (2.8). This results in the minimum amount of CO_2 that has to be fed into the system during the process to eliminate Li_2O generation and to ensure a rapid conversion of Li_2O back to carbonates. (Peng et al., 2017)

If CO₂ electrolysis is used to produce some form of a carbon product instead of CO, the product has to be somehow removed from the cathode. This means that the cathode has to be lifted from the electrolyte for the removal process. Since the electrolyte is heated to at least 750°C and is highly corrosive, when implementing a process where production is continuous, a way to remove the product from the electrolysis chamber has to be considered. After the cathode is emerged from the electrolyte, the end product has to be removed from the cathode, which can be accomplished by cooling the cathode to room temperature by simply removing the cathode from the electrolysis chamber and waiting, carefully removing the product from the cathode and washing the product with HCl or deionized water. The faradic efficiency of the whole electrolysis process approaches 100%, if the cleaning is done carefully and all of the end product is recovered (Licht et al., 2015).

Electrolysis stack is a method of electrolysis production where several electrolysis cells are either connected in parallel or series to reach greater production rates. For example, hydrogen is often produced using these compact yet efficient systems. Since CO₂ electrolysis technology is still a relatively new field of research, very little experimentation exists on the subject and most of the existing research focus on finding different means of controlling the resulting end product and how to overcome the material and heating challenges.

4 PROCESS MATERIALS IN CARBON DIOXIDE ELECTROLYSIS

Corrosiveness of the process electrolyte and the required high process temperature causes that the materials for electrolysis components, anode, cathode and container, has to be chosen carefully; they have to withstand 750°C temperature and corrosion for extended periods of time, preferably for the lifetime of the system. Especially the container material choice is of crucial importance; if the electrolyte manages to dissolve through the electrolysis container, it could cause serious safety and environmental issues. The choice of the electrolyte can save in thermal and electrical energy costs: different electrolytes have different conductivity characteristics and different melting points – electrolysis can be performed only in molten electrolyte.

4.1 Electrolyte

Using different kinds of molten salts in the CO₂ electrolysis has been widely researched. These molten salts consist of magnesium carbonate (MgCO₃), calcium carbonate (CaCO₃), barium carbonate (BaCO₃), sodium carbonate (NaCO₃), potassium carbonate (K₂CO₃), lithium carbonate (Li₂CO₃) and different mixtures of these. Out of these different electrolytes, the usage of Li₂CO₃ is the most common in existing CO₂ electrolysis studies. The preference of Li₂CO₃ as the process electrolyte can be explained with a low required cell voltage due to higher conductivity (6 S/cm) than that of the other salts, has a lower melting temperature meaning less thermal energy is required, can reach higher faradic efficiencies and CO₂ absorption rate into the electrolyte is 50 times higher than other carbonates. The cell voltages of different carbonate mixtures at different current densities using a stainless steel cathode and a nickel anode can be seen in Fig. 4.1. (Kanai et al., 2019) (Licht et al., 2010).

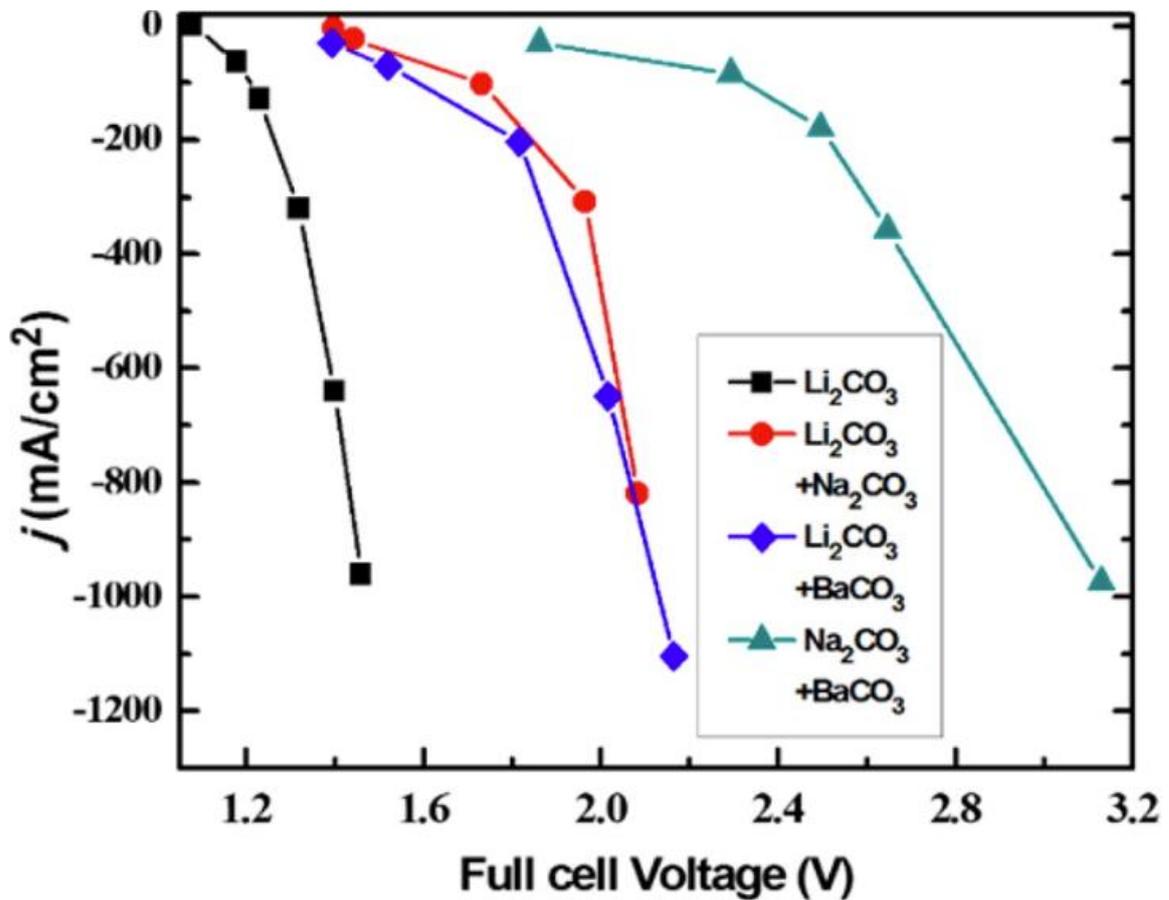


Figure 4.1. Cell voltages of different carbonates at different current densities. (Ren et al., 2015)

The price of Li_2CO_3 has been substantially increasing since 2010 due to its extensive applications in next generation technologies; in 2016 the price of Li_2CO_3 reached 20 000€ per ton and the price increase is a hundred times that of other salts (Yu et al., 2017). However, the price of electrolyte only adds an additional 130€ per ton production cost to the end product since a 10-year usage can be assumed and the electrolyte does not deplete (Licht et al., 2015).

4.2 Anode and Cathode

As for all the process materials, the anode material has to be chosen carefully to ensure that it is suitable for the electrolysis process, meaning the material should have adequate conductivity, and it withstands the high corrosiveness and heat of the electrolyte. Different options for anode materials that previous studies have found suitable for CO_2 electrolysis process in molten salts are nickel, titanium, platinum, iridium, graphite and stainless steel (Kaplan et al., 2013) (Peng et al., 2017) (Ijije et al., 2014). The material choice varies

depending on the preferred end product, the process temperature, material costs and material availability.

Nickel undergoes slight corrosion in molten Li_2CO_3 , but it can be used the anode material when the desired CO_2 electrolysis end product is CNTs, since the dissolving trace nickel can act as nucleation sites necessary for CNT production. This, however, means that the nickel anode has to be periodically replaced; the changing interval depends on the thickness of the anode – at 750°C and 100 mA/cm^2 current density with 0 mol/kg of Li_2O in the electrolyte the nickel loss is 0.5 mg/cm^2 in 600 s of electrolysis and with 5 mol/kg of Li_2O in the electrolyte the corrosion increases to 4.1 mg/cm^2 in 600 s of electrolysis. This trace nickel is deposited on the cathode, where it acts as nucleation sites for CNT formation. Nevertheless, the nickel loss in the electrolysis process is negligible if CO_2 feed into the system is ensured and the anode replacement interval is rather long. (Ren et al., 2015)

Cathode, unlike anode, is not exposed to the electrolyte for the whole electrolysis period, since the carbon product forms a protective layer on the cathode material. Nevertheless, same constraints affect the material choice for the cathode as for the anode: it has to be electrochemically suitable for the process, it has to have adequate conductivity, and it has to withstand the corrosiveness and the heat of the electrolyte. For the most part similar materials can be used as the cathode as the anode except for nickel, which should solely be used as the anode material due to its CNT production enabling characteristics.

4.3 Container

Container material choice is important since it has to withstand the electrolyte for several cycles of electrolysis without etching. In addition, the material should be well insulating to preserve the energy used in heating the electrolyte. Many previous papers have used an alumina crucible as the electrolysis container; it is a cheap and good option for CO_2 electrolysis when producing carbon products, when producing CO , higher temperature and increased Li_2O concentration level cause the alumina crucible to start corroding (Ren et al., 2015). Other valid material choices for the process container are corundum, titanium and nickel. If nickel is used as the container material choice, it can simultaneously act as the process anode. However, like in the case of anode material, if nickel is used as the container material, it will undergo some corrosion during the electrolysis process.

5 CARBON DIOXIDE ELECTROLYSIS PRODUCTS

Essentially, carbon dioxide electrolysis can be divided into two different splitting reactions: either CO or pure carbon is formed on cathode and oxygen is formed on anode. The basic reactions for these two conversions were presented in (2.2) and (2.3). The desired end product can be varied by changing the process temperature: for example, when using lithium carbonate (Li_2CO_3) as an electrolyte, at temperatures below 800°C the product is carbon and when the temperature rises, the amount of CO forming on the cathode increases. When the temperature reaches 950°C , the end product becomes pure CO. (Ren et al., 2015). Even though only the fundamentals of elemental carbon electrolysis production were presented in Chapter 2.1, a brief insight on CO production is given in this chapter, due to its possible utilization in the future energy system.

5.1 Carbon monoxide

New challenges emerge as renewable energy becomes more commonplace. For example, because of changes in weather and irradiation, both wind and solar PV power generation naturally fluctuate greatly even within shorter time periods and the effect is even more noticeable between seasons; solar PV power generation is much more abundant during summer months than it is during winter or autumn. This variation in power generation is the reason why different methods for storing excess energy generated during periods of greater power generation, for usage at periods of lower generation are being developed: supply and demand have to be in balance to ensure the grid stability, meaning the same amount of electricity has to be consumed as it is generated. Currently this stability is ensured by using water reserves and fossil power plants that are activated when more power is consumed than it is being generated. However, this stability could also be ensured by using different kinds of energy storages. These energy storages could be charged during times of excess power, such as daytime, and they could be used to match available energy to consumption at times when renewable generation is not as high, such as evenings and nighttime.

These days energy storages are still rather expensive to produce especially on a larger scale, and battery production uses a lot of toxic materials that have strong environmental effect. However, average battery prices have been lately steadily decreasing and the prices are expected to further decrease as the battery technology advances: for example, the U.S. Department of Energy Vehicle Technology Office has determined a target of \$125 per kWh

of electric vehicle battery storage by year 2022 (Licht et al., 2015). Electrochemically produced CO can be used as a fuel in a gas turbine as it is or it can be further processed into methanol, for example. This means that carbon dioxide electrolysis can be used to produce a form of an energy storage: electrolysis process can be run during times of excess power, such as during midday when irradiance is the highest, and the end product can be used to fuel electricity production when consumption is higher than production.

If CO₂ is bubbled into the system as a continuous stream, the reduction of CO₂ to CO can be run continuously. The reason for this is the gaseous form of the resulting pure CO that does not require further procedures for removing the product from the cathode. Instead, the product can be removed from the electrolysis cell as a continuous stream of gas (Kaplan et al., 2010). For example, when using Li₂CO₃ as the electrolyte, this continuous removal of the end product allows the following self-replenishing cycle for the electrolysis cell:



where (5.4) is the desired cathode reaction (Kaplan et al., 2013). Fig. 5.1. presents an example scheme of a continuous CO₂ to CO reduction system where O₂ formed on the anode and CO formed on the cathode are removed from the electrolysis cell during electrolysis.

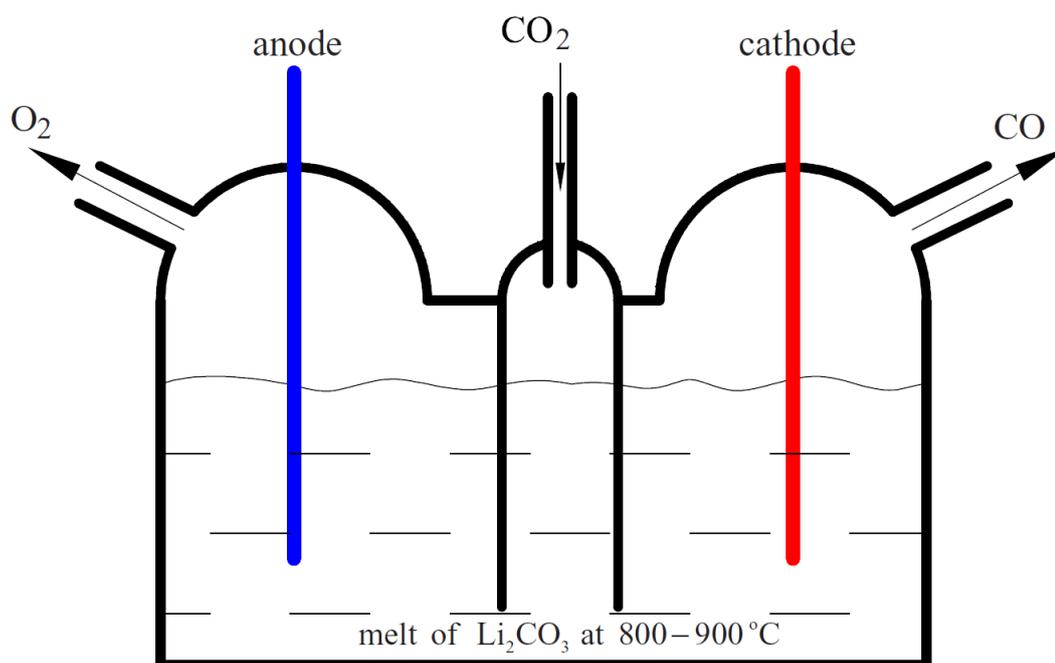


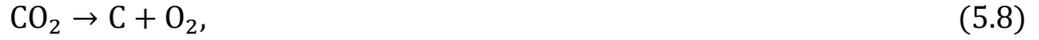
Figure 5.1. An example of a continuous CO₂ to CO reduction electrolysis system (Kaplan et al., 2010).

This is an advantage compared to the other end products, since in cases of solid carbon formation the cathode has to be removed from the electrolyte for the product removal.

A great disadvantage in producing CO is the nature of corrosiveness of the molten salts used as the electrolyte. To have pure CO without any elemental carbon as the end product, the electrolysis operating temperature must be maintained higher. For example, when using Li₂CO₃ as the electrolyte, the electrolysis temperature has to be at least 950°C to eliminate the possibility of cathode carbon formation. Higher the electrolysis temperature, higher the corrosiveness of molten salts, meaning that the choice of the used materials becomes more crucial. (Sridharan & Allen, 2013).

5.2 Carbon structures

At temperatures below 950°C carbon dioxide electrolysis end product shifts gradually from CO to carbon and at temperatures below 800°C the product forming on the cathode is purely carbon. Lower temperature means that the process does not face such immense feasibility problems when choosing anode, cathode and container materials, as in the case of CO production due to lower corrosiveness of the electrolyte carbonate. Electrochemical cathode and net reactions for elemental carbon production are as follows:



where C can be formed in different carbon structures by altering the process conditions. (Peng et al., 2017).

Electrolysis in molten salts can be used to form various different carbon structures. These structures include amorphous carbon, graphene, spherical carbon particle powder, nanostructured carbons including carbon nanofibers (CNFs) and carbon nanotubes (CNTs) (Douglas & Pint, 2017). The forming carbon structures can be controlled by varying different process conditions such as temperature, electrolyte, electrode materials, variation in current density and by adding additional Li_2O and nucleating metals, such as nickel (Ni), copper (Cu), cobalt (Co) or iron (Fe) (Ren et al., 2015). These condition variations can be used to manage the carbon product forming on the cathode and necessary process conditions for some carbon end products can be seen in Fig. 5.2.

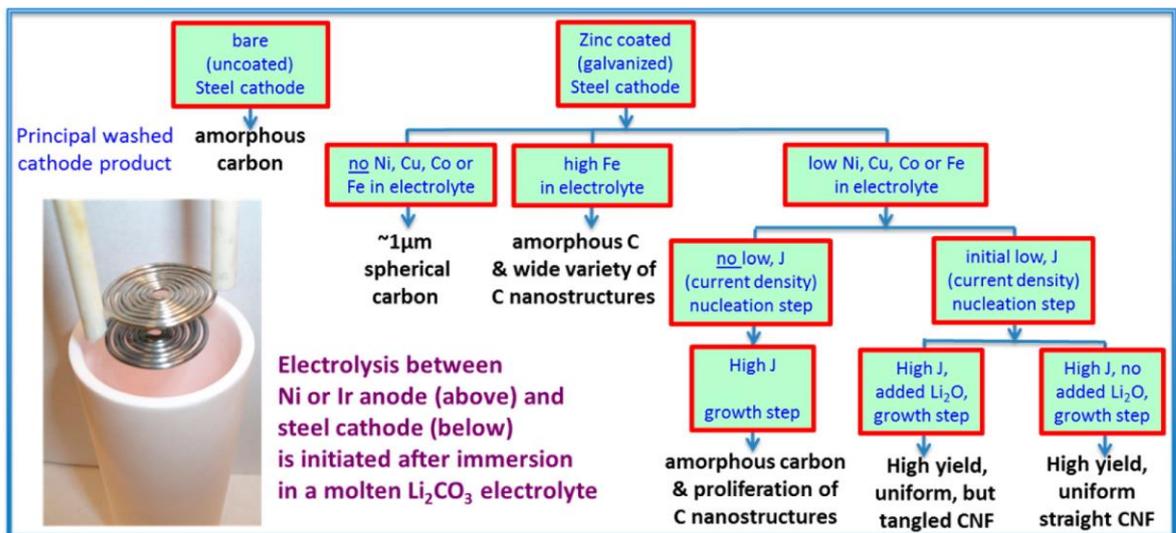


Figure 5.2. Pathways to different end products in molten carbonate electrolysis (Ren et al., 2015).

Differences in material characteristics and challenges in production cause that the products have great variation in price, meaning that production of some materials might be more economically feasible than the production of others. Average selling prices and market sizes

of different elemental carbon structures in 2016 can be seen in Table 5.1. (Douglas & Pint, 2017):

Table 5.1. Average selling prices and market sizes of different carbon structures in 2016.

Voltage (V)	Price (€/kg)	Market size (bn €)
Carbon fiber	20.0	6.79
CNTs	9043	7.32
Carbon black	1.11	25.37
Graphene	2261	1.90
Activated carbon	0.32	10.15

Since the carbon product is formed in a solid form on the cathode, the cathode has to be removed from the electrolyte for removal and cleaning of the product. The removal can be achieved by cooling the electrode to room temperature and carefully removing the product from the cooled cathode. After removal the product can be cleaned with deionized water or hydrochloric acid (HCl) after which the product is separated from the cleaning solution by paper filtration or centrifugation (Ren et al., 2015). This can be considered a significant disadvantage compared to the CO production, since CO₂ electrolysis cannot be run continuously causing the implementation of an electrolysis stack becoming more difficult.

5.2.1 Carbon fiber

Carbon fibers consist almost exclusively of carbon atoms and are the strongest fibers that are currently used to reinforce polymeric matrices; they display tensile strength of over 6 GPa while being light and having a low density (1.8–2.0 g/cm³). They are also highly thermally conductive (1000 W/mK) and somewhat electrically conductive. The characteristics are highly dependable on how they are used—carbon fiber is rarely used alone, instead it is combined with other materials to act as a reinforcing element. Due to the characteristics of carbon fibers they are extensively used in aerospace grade composites. (Jeon et al., 2013).

There are currently three popular carbon fiber production methods:

- polyacrylonitrile (PAN) process

- Pitch-based process
- Vapor-growth process.

Carbon fiber production is a well-known and studied field; the first carbon fibers were produced as early as 1860. About 90 % of carbon fibers are produced using the PAN process, where PANs are first spun into PAN fibers, which are then stabilized in air at 200–300°C. Afterwards, these stabilized PAN fibers are carbonized in inert atmosphere at 1200–1400°C which produces tightly bonded carbon crystals which are finally treated at high temperatures (2000–3000°C) to form high-performance (HP) grade PAN-based carbon fibers. (Inagaki, 2000).

PAN process requires more energy than pitch-based processes, but it produces carbon fibers with superior properties, such as higher tensile strength. PAN based process average cost of non-aerospace grade carbon fiber sits at around 20 €/kg, which is highly dependable on the cost and yield of precursor from which it is obtained (Rao et al., 2018). The amount of energy consumed during the production process is also crucial when considering the total production costs. By current methods the typical production energy is 315 kWh per kilogram of carbon fiber produced, which is relatively high compared to average production energy of aluminum; the average production energy of aluminum is about 15 kWh per kilogram of aluminum produced. The production energy of carbon fibers can be reduced by optimizing the production process and it is estimated that the practical minimum could be as low as 92 kWh per kilogram of carbon fiber produced. (Sunter et al., 2015).

5.2.2 Amorphous carbon

Amorphous carbon is a reactive carbon structure that does not possess a long-range crystalline order. Some short-range orders can be observed, but with deviations with respect to the graphite lattice. (Marsh et al., 2006).

One example of amorphous carbons is carbon black, which is a form of paracrystalline carbon with a low volume to surface area ratio. Carbon black has various uses in the industry due to its material characteristics: it is both electrically and thermally conductive, it absorbs ultraviolet radiation and it is a good pigment due to its low surface area to volume ratio. There are other amorphous carbon products, like activated carbon, and the products have various uses due to their unique and superior properties. These uses include applications for

plastic, healthcare and textile industries as well as in the fields of water and gas filtering, food packaging and electrical applications. (Ho & Lau, 2015).

Production methods of different amorphous carbon structures are relatively similar, and they can be produced primarily by incomplete combustion of plant or animal substances. For example, carbon black is produced in four different methods:

- Channel process
- Furnace black process
- Lampblack process.
- Acetylene black process

The most commonly used process is the furnace black process where petroleum, coal oil or oil is used as raw material which are blown into hot gases to ignite them partially. The process can be run continuously, because there is no need to change the equipment or feedstock. (Mitsubishi, 2006). Amorphous carbon is one of the cheapest carbon structures due to the simplicity of its production.

5.2.3 Graphene

Graphene is a two-dimensional carbon structure with unique and intriguing properties. It is the essential element of other carbon structures like graphite, fullerene and CNT. Graphene has many diverse forms due to its flexibility. For example, in addition to its basic continuous hexagonal mesh structure, graphene is the most commonly formed into a monolayer sheet of high-strength graphene. By stacking two of these layers results in a bilayer graphene form. (Holkar et al., 2018). The chemical structure of basic continuous graphene can be seen in Fig. 5.3.

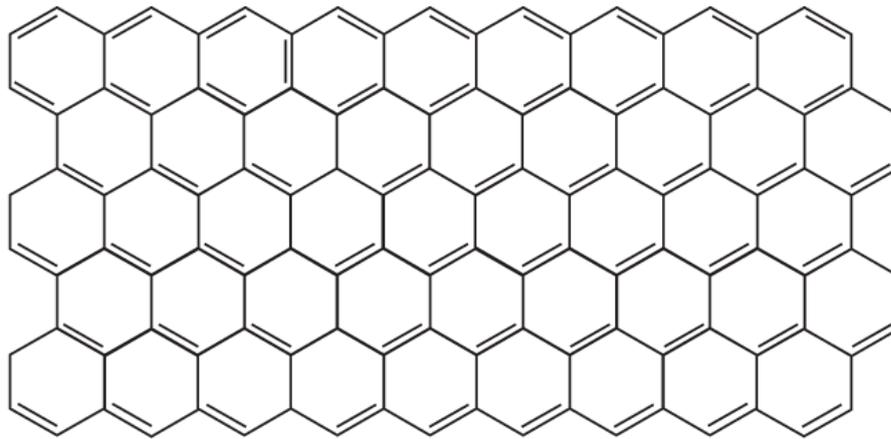


Figure 5.3. Structure model of graphene (Matesh et al., 2015).

Graphene has many superior characteristics making it a desirable material for several different applications such as energy storage and generation, medical and biomechanics. It is:

- One of the strongest materials on earth; it has a tensile strength of 130.5 GPa
- Ideal material for spintronics, where spin of the electron and its magnetic moment is transformed between electrodes
- A great electric charge carrier due to its unique nature of electron transfer rates and much more (Novoselov et al., 2008) (Warner et al., 2013).

Graphene has several different production mechanisms, but it is currently produced in four common methods:

- Mechanical exfoliation
- Exfoliation by graphite oxide reduction
- Sonication
- Epitaxial carbon vapor deposition.

Different production methods have different advantages. For example, the mechanical exfoliation method is a method that utilizes scotch tapes, it is extremely simple and cheap production method, but it lacks control on the production. Meanwhile the sonication process is a costly, energy-intensive process, but it provides strong control on the resulting graphene size. (Holkar et al., 2018). Due to the high costs of these different production methods and the great material characteristics, graphene can be considered an interesting CO₂ electrolysis

end product option; electrochemical reduction of CO₂ could act as a new cheaper alternative for existing production techniques.

5.2.4 Carbon nanotubes

CNTs are nanoscale tubular carbon atom structures that have a diameter measured on a nanometer scale but a length of some micrometers which possess a tensile strength of about 63 GPa (Purohit et al., 2014). Ideal, atomically perfect CNTs are described to be 100 times stronger than stainless steel while being six times lighter, hard as diamond while maintaining thermal capacity double that of pure diamond, conductivity 1000 times higher than that of copper and thermally stable up to 4000 K (Qian et al., 2002). However, production of ideal CNTs is impossible using the current production methods, but even the unideal CNTs maintain some of these exceedingly superior characteristics enabling various applications where CNTs can be used. These applications include technologies such as spacecraft applications, medicine, electronics, energy storage, automotive and so on.

Currently CNTs are produced in three popular processes:

- Arc discharge
- Chemical vapor deposition (CVD)
- Laser ablation.

All of these methods are based on providing energy to a carbon source where created carbon atoms generate CNTs. Energy sources in these methods are current, high intensity light and heat, respectively (Purohit et al., 2014). Despite huge advancements in CNT research over the years, the production of CNTs in large quantities using these popular methods is still difficult and non-cost-effective; current production processes require 30–100 times higher production energy than that of aluminum (Ren et al., 2015). Nevertheless, the synthesis of CNTs is gaining interest due to the various applications and ongoing research enabled by its material characteristics.

CNTs can be divided into five different type based on structural differences. These different types of structures are:

- Single walled carbon nanotubes (SWCNT), which are single walled, have 1 nanometer diameter.

- Multi walled carbon nanotubes (MWCNT), which consist of several layers of graphite rolled on each other to form a tubular shape.
- Polymerized SWCNTs, which are a solid-state formation of fullerenes and related compounds. In this case, many SWCNTs intertwine to form a polymerized SWNT structure, which has a hardness level comparable to that of a diamond.
- Carbon nanotorus, which is a carbon nanotube bent into a donut shape. They have many unique characteristics, such as magnetic moments a thousand time larger than expected from such nanoscale structure.
- Carbon nanobuds, which are a recently discovered material that are formed by combining two known allotropes of carbon: CNTs and fullerenes. (Purohit et al., 2014).

The atomic structures of these different CNT types are depicted in Fig. 5.4.

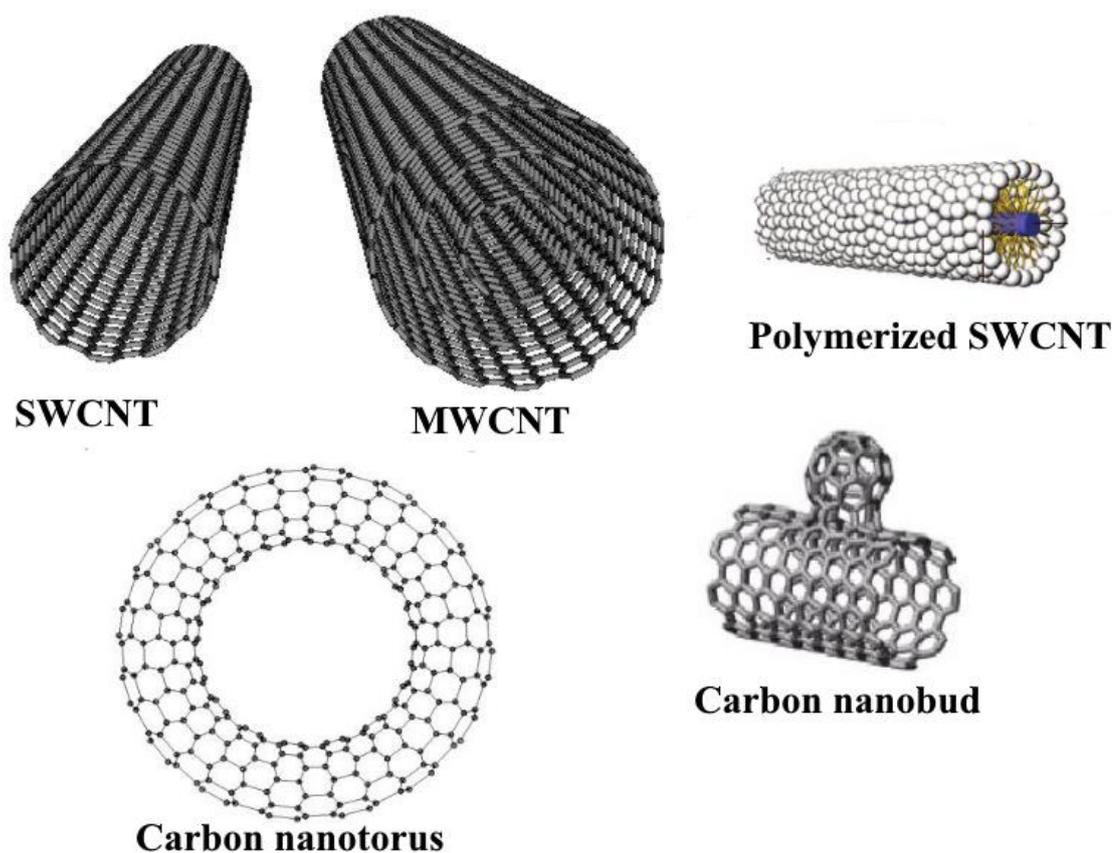


Figure 5.4. Structural models of different CNT types (Tepfers, 2008) (Okwundu et al., 2018) (Do & Jang, 2013) (Reddy et al., 2009).

CNT is the most expensive carbon structure manufactured via electroreduction of CO₂. Carbon dioxide electrolysis could provide a solution for CNT synthesis; by producing CNTs

via electrolysis in molten carbonates, assuming 0.9 to 1.4 V cell voltage, the electrical energy usage in the electrolysis process would be 8000 kWh to 16000 kWh per metric ton of produced CNT. Li_2CO_3 used as the electrolyte in the electrochemical reduction process is valuable, but it does not diminish in the electrolysis process if sufficient CO_2 feed is provided, meaning that at least a 10-year lifetime can be assumed. This means that the usage of expensive electrolyte would not affect the production costs notably and can be ignored. These costs are a fraction of the current CNT production costs; by current methods the production costs of industrial grade CNTs vary between 179 000 € and 359 000 € per ton depending on the CNT type produced, meaning CO_2 electrolysis could provide a cost-effective method for CNT production. (Licht et al., 2016).

5.3 Product conclusion

Current production costs for different carbon end products vary greatly. However, the production costs when using the electrochemical reduction of CO_2 to produce these materials is dependent only on the process energy consumption, which varies only slightly between the different carbon products. The most prominent difference emerges when comparing the heat energy requirements between CO production, which requires higher process temperature, and carbon structure production, where the process temperature is lower. This means that the production costs of different carbon structures can be assumed to be equal, meaning that producing otherwise expensive materials via CO_2 electrolysis is more worthwhile than producing materials such as carbon black or carbon fiber.

5.3.1 Product energy requirements

Production of carbon materials consume electrical energy in sustaining the cell voltage in the electrolysis cell, and heat energy to sustain the 750°C process temperature.

To sustain a 1.4 V process cell voltage, the electrical energy consumption would be around 16 kWh per kilogram of carbon material produced according to values found in literature. (Licht et al., 2016). This value is similar in all the different elemental carbon products, since the process conditions varies only slightly between different end products.

As for the required heat energy for a kilogram of carbon material produced, the situation is a little more complicated since there are several conditions affecting the energy requirement.

Enough heat energy has to be supplied into the system to replenish the energy lost from the system. Heat losses in the system are illustrated in Fig. 5.5. below. The energy lost on removing resulting hot carbon product is disregarded, since it is done only periodically, and the energy loss is considered minimal.

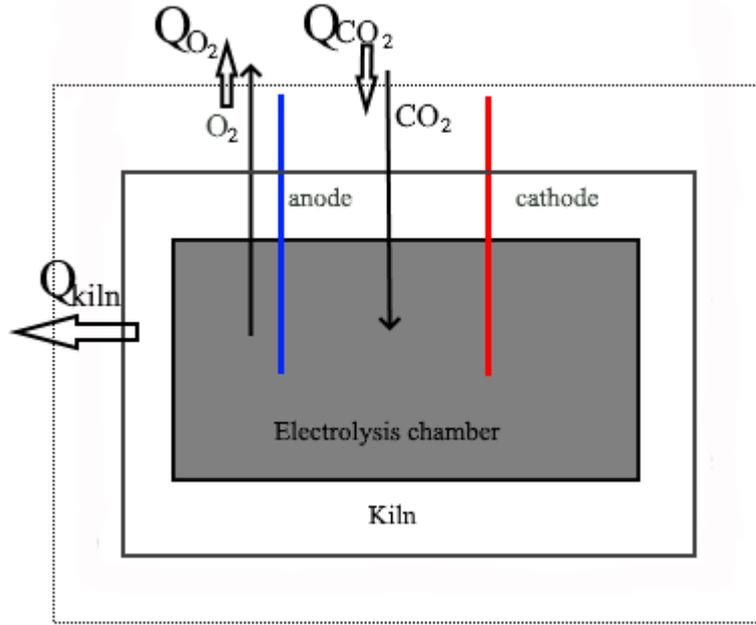


Figure 5.5. Heat loss from the electrolysis system.

According to Fourier's Law of heat conduction, the heat loss of the kiln (W) can be calculated as follows:

$$Q_{kiln} = \frac{k_w A (T_{hot} - T_{cold})}{d}, \quad (5.9)$$

where k_w is the thermal conductivity of the wall, A is the area of the kiln wall subject to heat loss, T_{hot} is the inside temperature, T_{cold} is the outside temperature and d is the diameter of the wall. Thermal conductivity of typical insulated fire brick is around 0.5929 W/mK (Peng et al., 2017). To simplify the calculations, it is assumed that the electrolysis chamber is completely surrounded by kiln, but in reality, the kiln should have openings for CO_2 feed, O_2 and end product removal, and heat generation. In the simulation that Peng et al., 2017 performed, the electrolysis cell was surrounded by Paragon Fusion 16 kiln, parameters of which are presented in Table 5.2 below together with parameters used in the calculations.

Table 5.2. Parameters of the used kiln and parameters used in calculations (Paragon, 2011).

k_w	0.5929 W/mK
A	0.5976 m ²
d	0.257m
T_{hot}	750°C
T_{cold}	25°C
c_{pO_2}	1.054 J/gK
v_{O_2}	0.317 mmol/s
M_{O_2}	32 g/mol
T_{O_2}	750°C

Since the structure of the kiln consisted mainly of firebricks his means that the total heat loss of the kiln is according to (5.9).

$$Q_{kiln} = \frac{0.5929 \frac{W}{m \cdot K} \cdot 0.5976 m^2 \cdot (750 - 25)K}{0.257 m} = 999.53 W.$$

However, a larger electrolysis chamber than that of in simulations performed by Peng et al., could be fit inside the kiln in question decreasing the heat loss per unit of product produced, but this paper uses these values as an example for production energy requirements.

Removal of the oxygen generated on the anode removes heat from the system at following rate (W):

$$Q_{O_2} = c_{pO_2} v_{O_2} M_{O_2} T_{O_2}, \quad (5.10)$$

where c_{pO_2} is the specific heat capacity of oxygen at 750°C, T_{O_2} is the temperature of the oxygen being removed from the system, M_{O_2} is the molar mass of oxygen and v_{O_2} is the rate of oxygen being generated on the anode, which is the same as the production rate of the system. The rate of oxygen being generated on the anode is the same as the rate of carbon being generated on the cathode, and according to Peng et al., 2017, the maximum theoretical production rate of a system with effective cell area of 612 cm² and current density of 200

mA/cm^2 is 0.317 mmol/s. This means, that according to (5.10), the heat loss caused by oxygen removal is

$$Q_{O_2} = 1.054 \text{ J/gK} \cdot 0.317 \text{ mmol/s} \cdot 32 \text{ g/mol} \cdot (273.15 + 750) \text{ K} = 10.9 \text{ J/s} \\ = 10.9 \text{ W}$$

Some of this heat loss can be recovered by using this heat to preheat the CO_2 fed into the system by using a heat exchanger, but the heat loss caused by the removed oxygen is small compared to the total heat loss, meaning that the heat exchanger might not be worth the cost.

Total heat loss in the process to produce 0.317 mmol/s of carbon product is

$$Q_{\text{tot}} = Q_{\text{kiln}} + Q_{O_2} = 1010 \text{ W} \quad (5.11)$$

With carbon molar mass of 12.0107 g/mol and production rate of 0.000317 mol/s, the maximum theoretical carbon product generation rate at these conditions is 0.00381 g/s. By using the total heat loss and the production rate, the heat energy required to produce a kilogram of end product (kWh/kg) can be calculated as follows:

$$E_{\text{heat}} = \frac{1010 \text{ W}}{0.00381 \text{ g/s}} = 265\,091 \text{ Ws/g} = 73.63 \text{ kWh/kg}. \quad (5.12)$$

This is the total heat energy lost from the system, which has to be replenished to maintain the process temperature of 750°C. This can be achieved by using an external heat source. However, some of the heat can be produced by bubbling CO_2 into the system during the electrolysis process. As been stated in Chapter 2.1.1, reaction (5.10) releases 158 kJ/mol of energy into the system if the fed CO_2 is preheated to 750°C. A kilogram of end product has 83.26 moles of carbon, meaning 83.26 moles of CO_2 can be fed into the system when producing one kilogram of end product. This means that feeding CO_2 into the electrolyte generates

$$E_{\text{CO}_2} = 83.26 \text{ mol/kg} \cdot 158 \text{ kJ/mol} = 13\,155 \text{ kJ/kg} = 3.65 \frac{\text{kWh}}{\text{kg}} \quad (5.13)$$

of energy. This decreases the amount of external heat required, meaning that the amount of external heat required to maintain the process temperature is

$$\begin{aligned} E_{\text{ext}} &= E_{\text{heat}} - E_{\text{CO}_2} \\ &= 73.63 \text{ kWh/kg} - 3.65 \text{ kWh/kg} = 69.98 \text{ kWh/kg}. \end{aligned} \quad (5.14)$$

In addition to this heat energy, heat energy is required to heat the process kiln from 25°C to 750°C in the beginning of the process. However, after the initial heating, the process can be run continuously, meaning that the initial heating energy requirement is rather low compared to the total energy required.

5.3.2 Product costs

The energy requirements to produce carbon products via CO₂ electrolysis are summarized in Table 5.3 below together with current market prices of these products. Energy consumption in different carbon material production processes are assumed to be same in this paper, since the production conditions varies only marginally between different end products. Actual values for heat energy required for a kilogram of product produced might be lower, since the calculations were performed on a system on which the kiln was much larger than required for the electrolysis chamber, meaning bigger heat losses. The amount of heat energy can be affected by better insulation and by increasing the system size. However, when comparing the energy requirements to the current market prices of the carbon materials, it is clear that this alternative production method is still considerably cheaper when producing CNTs and graphene.

Table 5.3. 2019 market prices of different carbon dioxide electrolysis products, and CO₂ electrolysis electrical energy usage and heat energy usage.

	Market price (€/kg)	Electrolysis electrical energy usage (kWh/kg)	Electrolysis heat energy usage (kWh/kg)
Carbon fiber	20.0		
CNTs	9043		
Carbon black	1.11	16.0	69.98
Graphene	2261		
Activated carbon	0.32		

When comparing electrical and heat energy consumed to produce carbon products via CO₂ electrolysis to the current market prices of different carbon materials, it is clear that the production of some carbon structures via CO₂ electrolysis is a great alternative for material production. It is obvious that producing CNTs or graphene using CO₂ electrolysis is much more economically feasible than producing other materials, such as carbon black or activated carbon. However, the option of using CO₂ electrolysis to produce materials beside the most economically feasible ones should not be neglected either.

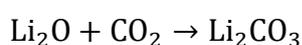
6 EXISTING TECHNOLOGIES

Since CO₂ electrolysis is still relatively new field of research, most of the existing systems are focused on finding the best methods of producing different materials and how to overcome different production challenges. This means that at the time of writing this paper, no commercially available systems exist, and the CO₂ electrolysis is not used to produce carbon materials on a notable scale. This chapter discusses already realized systems, illustrates the working methodology of said systems and considers the possible future of CO₂ electrolysis.

6.1 Carbon monoxide

Several research papers have investigated the possibility of CO production in CO₂ electrolysis. As been mentioned previously, CO can be produced in a continuous manner via CO₂ electrolysis; CO₂ can be continuously bubbled into the electrolyte to rapidly convert Li₂O back to Li₂CO₃ and the gaseous end product can be removed from the cathode through an outlet and the end product requires no further cleaning. Continuously bubbling CO₂ also ensures that the formation of highly corrosive Li₂O is minimal. Feeding excess CO₂ does not interfere with the process, but sufficient CO₂ bubbling should be ensured. Thus, the outlet CO flow should be continuously measured to determine the minimum amount of CO₂ required to convert all of the forming Li₂O back to Li₂CO₃.

The most common electrolyte in existing studies when producing CO via CO₂ electrolysis is Li₂CO₃. Other molten salts have been experimented and their different mixtures have been studied to find a replacement option for expensive Li₂CO₃. However, most studies agree that Li₂CO₃ is the most valid option for the electrolyte despite high material costs; a 10-year lifetime can be assumed for the process electrolyte, meaning the electrolyte price does not affect the production costs significantly. Li₂CO₃ is typically heated to 900–950°C to ensure that no carbon structures form on the cathode. The process temperature is monitored to ensure that no elemental carbon forms on the cathode, which might interfere with CO production. If CO₂ is bubbled into the electrolyte during the process, the fact that reaction



is exothermic, meaning it produces heat into the system, should be taken into consideration when introducing external heat into the electrolysis chamber (Kaplan et al., 2010).

At these temperatures the electrolyte is very corrosive and it can dissolve materials such as platinum and gold. Therefore, the material choice becomes a very crucial task when preparing the CO₂ electrolysis system setup. Typical existing setups use titanium, graphite and iridium as their container, inlet and outlet tube, and anode and cathode materials, since these are materials that do not corrode under the electrolysis conditions. (Kaplan et al., 2010) (Kaplan et al., 2014)

If the electrolyte is not contaminated and the CO₂ bubbled into the electrolyte is pure, the faradic efficiency of this process is close to 100% at current densities ranging between 100–500 mA/cm². As typical for electrolysis processes with gaseous products, the thermodynamic efficiency is high due to positive process entropy, and thermodynamic efficiencies of above 85% have been observed. (Kaplan et al., 2010) (Kaplan et al., 2014)

If the produced CO were converted back to electricity with anodic re-oxidation in the same molten salts as it was produced, as high as 95% charge efficiencies can be reached. Since CO can be easily stored, this high charge efficiency promises great seasonal energy storage opportunity (Ijije et al., 2014).

6.2 Carbon structures

More research is being focused on developing CO₂ electrolysis focused on different carbon structures because of the different applications of these valuable carbon materials than is being focused on CO production based electrolysis. CO₂ electrolysis has been successfully used to produce following carbon structures:

- Amorphous carbon
- Graphene
- Spherical carbon structures
- Carbon nanofibers
- Carbon nanotubes

and especially the production of various carbon nanostructures via CO₂ electrolysis has been researched actively lately.

As in the case of CO production, Li_2CO_3 is the most commonly used process electrolyte, and CO_2 can be bubbled into the electrolyte in carbon structure production to replenish the carbon deposited during the electrolysis process. However, here the production cannot be run continuously, for the solid electrolysis product has to be manually removed from the cathode. A typical existing experimental setup removes the cathode from the electrolyte, waits for the electrode to cool down and uncoils it which causes the product to fall off from the electrode. After the removal, the product is typically washed with deionized water or hydrochloric acid and filtered. (Ren et al., 2015).

Currently typical carbon structure producing CO_2 setups run only for one cycle, meaning once the cathode is removed from the electrolyte for the cleaning process, the electrolysis process is stopped. If CO_2 is bubbled into the electrolyte to replenish the electrolyte and no Li_2O manages to form in the electrolyte, another cathode could be inserted into the molten salt and the electrolysis process can be started again.

However, it is worth noting that when producing CNTs the initial low current density required to form CNT nucleation sites on the cathode has to be performed after each new cathode insertion to enable CNT growth. CNT nucleation site formation requires also a nucleating metal, such as nickel (Ni), copper (Cu), cobalt (Co) or iron (Fe), out of which nickel is used the most commonly (Ren et al., 2015). The nucleating metal can be introduced into the electrolysis system as an additional element, or it can be used as the anode material. If the nucleating metal is introduced into the electrolysis system as anode material, the anode has to be periodically replaced due to corrosion caused by the electrolyte (Ren et al., 2015). CNT growth can be further controlled by adding additional 4 moles of Li_2O into one liter of electrolyte; with the added Li_2O tangled CNTs are generated, while straight CNT structures are generated without added extra Li_2O (Licht et al., 2016). Other ways of affecting the resulting end product can be seen in Fig. 5.2.

Here the process temperatures are a little bit lower, 700–750°C, than in CO production process, meaning that the electrolyte does not become as corrosive as in the case of CO production. This means that the process material selection is a little bit broader; for example,

an alumina crucible could be used which is a cheap and good material alternative for electrolysis container due to its material properties (Ren et al., 2015).

Faradic efficiencies of at least 80 % have been observed in the carbon production process, increased to near 100 %, if the end product is separated from the cathode perfectly, the product is cleaned with HCl or deionized water and finally is filtered to obtain all the product formed on the cathode (Licht et al., 2015) (Licht, 2015) (Ren et al., 2015).

The possibility of using exhaust fumes of a coal powered power plant has been experimented. If the bubbled CO_2 contains impurities, such as sulfur, the contamination typically forms at the cathode in solid form. These impurities reduce the faradic efficiency of the process, but to not less than 90%, meaning even with impurities the efficiency is satisfying (Kaplan et al., 2013). An example scheme of a combined STEP–Coal power plant is presented in Fig. 6.1.

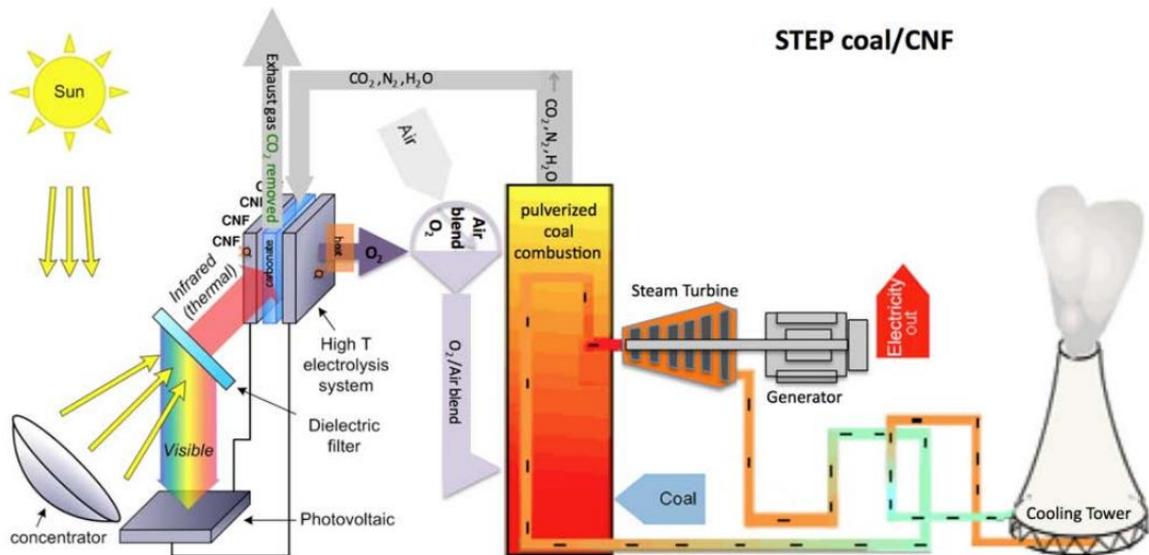


Figure 6.1. Combined STEP–Coal power plant (Licht, 2015).

CO_2 electrolysis used to produce different carbon structures could be used to produce otherwise expensive carbon materials in a cost-efficient manner. Especially the production costs of carbon nanostructures could be lowered significantly with this new emerging technology. This combined with the aspect of using otherwise unwanted atmospheric CO_2 gives great opportunity for different technological applications of CO_2 electrolysis.

7 DISCUSSION

Since the amount of atmospheric CO₂ is increasing and becoming a greater problem each day, a method to utilize this otherwise unwanted gas is highly desirable. CO₂ electrolysis is able to transform this greenhouse gas into valuable carbon materials that can be used in different applications. Currently both carbon and CO end products are produced mainly only for research purposes and finding the optimal process conditions, and no system exist solely for production reasons. In the future, however, this could change; especially the electrochemical reduction of CO₂ into different carbon structures shows great potential as an alternative in carbon material production. For example, existing CNT and CNF production methods are quite expensive due to high energy requirements

The production of CO is more expensive compared to elemental carbon due to higher process temperature, while the end product can be considered less valuable. However, using CO₂ electrolysis to produce CO could provide an alternative method to help balancing supply and demand differences caused by the great fluctuation of renewable energy production methods, such as solar PV, that are going to be used in the future in a much larger scale to meet the emission goals agreed upon in the Paris agreement.

In the future, the process efficiency can be increased via different process improvements. One such improvement could be using hot O₂ forming on the anode to preheat the CO₂ gas feed, which would decrease the heat energy required to upkeep high process temperatures. With better process efficiency, the production costs of the carbon materials could be further decreased making way for even more different applications and different methods of balancing the energy supply and demand.

All in all, the technology is promising, with climate change becoming more of a problem and new agreements being signed upon, its usage most likely will become more widespread with its great promise for CO₂ utilization. The next step is to move from research-based systems to more production focused systems and start experimenting with ways to increase the energy efficiency of the CO₂ electrolysis system.

8 CONCLUSION

The amount of atmospheric CO₂ has been steadily increasing since the industrial revolution in 1880s causing the average surface temperature to increase. This has caused several agreements to be signed limiting the increase of the average surface temperature, for example, the Paris Agreement in 2015, where 195 countries agreed to the goal of keeping the average surface temperature increase below 2°C above pre-industrial temperatures. Most of the countries have agreed to achieve these goals by transitioning from polluting fossil fuels to cleaner renewable energy sources. However, many sources agree that because of vast past and present greenhouse gas emissions the energy transition alone is not enough to maintain the average surface temperature below the agreed levels. This means in addition to transitioning to renewable energy sources, technologies that reduce the atmospheric CO₂ concentration are required to limit the temperature rise within the target range. One example of such technology is direct air capture, which captures CO₂ directly from air. This captured CO₂ contains oxygen and carbon, which are important elemental building blocks for different technological systems, meaning that the captured CO₂ can be further utilized as fuels or other materials. This utilization could be accomplished via electrochemical reduction of CO₂, aka CO₂ electrolysis.

The objective of this thesis is to carry out a literature review of state-of-the-art of high temperature CO₂ electrolysis technology and to discuss existing CO₂ electrolysis systems and ponder the future of the technology. CO₂ can be split into carbon monoxide or different carbon structures and oxygen, depending on the desired splitting reaction, by conducting direct current between to electrodes immersed in an electrolyte. The most commonly the CO₂ splitting reaction is carried in liquid molten salts in high temperatures, such as in lithium carbonate in 750–950°C. In lithium carbonate, pure carbon monoxide is produced at temperatures over 900°C from where the end product gradually shifts to carbon structures and by 800°C the end product is pure carbon.

Carbon monoxide is typically produced at 950°C in lithium carbonate and it can be produced in a continuous manner, since the product forming on the cathode is in gaseous form and can be removed from the electrolyte simultaneously with the electrolysis process. However, if the process is run continuously, it is of utmost importance to ensure sufficient CO₂

electrolyte to replenish the lithium carbonate and to ensure that no lithium oxide forms in the electrolyte since lithium oxide is more corrosive and has higher melting point than lithium carbonate. Electrochemically produced CO can be used as a fuel in a gas turbine as it is or it can be further processed into methanol, for example. This means that carbon dioxide electrolysis can be used to produce a form of an energy storage: electrolysis process can be run during times of excess power, such as during midday when irradiance is the highest, and the end product can be used to fuel electricity production when consumption is higher than production.

Carbon structures are typically produced at 750°C in lithium carbonate. The forming of carbon structure can be controlled by varying different process conditions, such as adding nucleating metals into the electrolyte or by altering the process current density. These forming carbon structure options include materials such as carbon nanofibers, carbon nanotubes and graphene. Electrochemically produced carbon structures have many different applications depending on the produced carbon structure and using carbon dioxide electrolysis to produce some carbon structures could decrease the production costs of said material. For example, producing carbon nanotubes using carbon dioxide electrolysis could lower the price of this otherwise expensive carbon material significantly. The applications of materials that could be produced using this electrochemical reduction are broad. Carbon structure production has a downside: since the product forming on the cathode is formed in solid form, the cathode has to be removed from the electrolyte and cleaned periodically meaning that a continuous production is harder to achieve.

Since the electrolysis process is typically performed in high temperature molten salts brings up several challenges with the process, such as how heating of the system is achieved and how to counteract the corrosive nature of these high temperature salts. Especially when producing carbon monoxide, which requires higher process temperatures than carbon structure production, the corrosiveness of high temperature electrolyte becomes a significant problem. For example, at 950°C lithium carbonate will dissolve through alumina, gold and platinum. At lower temperatures, such as at 750°C where the electrolysis process is performed when producing carbon structures, platinum and gold materials do not exhibit etching or mass loss. Problems caused by corrosion can be overcome with proper material selection and by following necessary process safety precautions.

Currently most of the production is research-based production and is mostly concentrated on finding optimal process conditions and searching for methods of affecting the resulting end product. However, more and more research are being focused on process energy efficiency and sustainability. In the future the technology could develop into more production based and carbon materials could be produced via electrochemical reduction of carbon dioxide in much more economically feasible way than they are produced with current production methods.

REFERENCES

- (Bessarabov & Millet, 2018) Bessarabov, D., Millet, P., 2018, "Chapter 2 – Brief historical background of Water Electrolysis" in: *PEM Water Electrolysis*.
- (Climate, 2018) *Climate Change: Atmospheric Carbon Dioxide*, Climate.gov, viewed 31.07.2019, <https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide>
- (Do & Jang, 2013) Do, C., Jang, H., 2013, "Hydration forces between surfaces of surfactant coated single-walled carbon nanotubes", *The Journal of Chemical Physics*, vol 138, no. 11.
- (Douglas & Pint, 2017) Douglas, A., Pint, C., 2017, "Review–Electrochemical Growth of Carbon Nanotubes and Graphene from Ambient Carbon Dioxide: Synergy with Conventional Gas-Phase Growth Mechanisms", *ECS Journal of Solid State Science and Technology*, vol 6, no. 6, pp M3084–M3089.
- (Europa, 2016) *Paris Agreement*, Europa.eu, viewed 02.08.2019, https://ec.europa.eu/clima/policies/international/negotiations/paris_en
- (Ho & Lau, 2015) Ho, M., Lau, A., 2015, "12– Amorphous carbon nanocomposites" In: Dong, Y., Umer, R., Lau, A., *Fillers and Reinforcements for Advanced Nanocomposites*, Elsevier.
- (Holkar et al., 2018) Holkar, R., Jain, S., Jadhav, A., Pinjari D., 2018, "Chapter 14– Scale-Up Technologies for Advanced Nanomaterials for Green Energy: Feasibilities and Challenges" In: Bhanvase, B., Pawade, V., Dhoble, S., Sonawane, S., Ashokkumar, M., *Nanomaterials for Green Energy*, Elsevier.
- (Hu & Suib, 2014) Hu, B., Suib, S., 2014, "Chapter 3– Synthesis of Useful Compounds from CO₂" In: Centi, G., Perathoner, S., *Green Carbon Dioxide Advances in CO₂ Utilization*, Elsevier.

- (Inagaki, 2000) Inagaki, M., 2000, “Chapter 4– Carbon fibers”, In: Inagaki, M., *New Carbons, Control of Structure and Functions*, Elsevier.
- (IPCC, 2014) *Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, viewed 01.08.2019, <https://www.ipcc.ch/report/ar5/wg3/>
- (Jeon et al., 2013) Jeon, Y., Alway-Cooper, R., Morales, M., Ogale, A., 2013, “Chapter 2.8 – Carbon Fibers”, in: Somiya, S., *Handbook of Advanced Ceramics (Second Edition)*, Elsevier.
- (Kanai et al. 2019) Kanai, Y., Terasaka, K., Fujioka, S., Fukunaga, K., 2019 “Absorption of Carbon Dioxide at High Temperature with Molten Akali Carbonate Using Bubble Column Reactor”, *Journal of Chemical Engineering of Japan*, vol 52, no 1, pp 31–40.
- (Kaplan et al., 2010) Kaplan V., Wachtel, E., Gartsman, K., Feldman, Y., 2010, “Conversion of CO₂ to CO by Electrolysis of Molten Lithium Carbonate”, *Journal of Electrochemical Society*, vol 157, no. 4, pp B552–B556.
- (Kaplan et al., 2012) Kaplan, V., Wachtel, E., Lubomirsky, I., 2012, “Titanium Carbide Coating of Titanium by Cathodic Deposition from a Carbonate Melt”, *Journal of The Electrochemical Society*, vol 159, no. 11, pp E159–E161.
- (Kaplan et al., 2013) Kaplan, V., Wachtel, E., Lubomirsky, L., 2013, “CO₂ to CO Electrochemical Conversion in Molten Li₂CO₃ Is Stable with Respect to Sulfur Contamination”, *Journal of The Electrochemical Society*, vol 161, no. 1, pp F54–F57.
- (Koponen, 2015) Koponen, J, 2015, “Review of water electrolysis technologies and design of renewable hydrogen production systems”, Master’s Thesis.
- (Licht et al., 2010) Licht, s., Wang, B., Ghosh, S., Ayub, H., Jiang, D., Ganley, J., 2010, “A New Solar Carbon Capture Process: Solar Thermal

- Electrochemical Photo (STEP) Carbon Capture”, *J. Phys. Chem. Lett.*, vol 1, no., 15, pp 2363–2368.
- (Licht et al., 2011) Licht, S., Wu, H., 2011, “STEP Iron, a Chemistry of Iron Formation without CO₂ Emission: Molten Carbonate Solubility and Electrochemistry of Iron Ore Impurities”, *J. Phys. Chem*, vol 115, no. 50, pp 25138–25147.
- (Licht, 2015) Licht, S., 2015, “Carbon Nanofiber (from fossil fuel) Electric Power Plants: Transformation of CO₂ Exhaust to Stable, Compact, Valued Commodities”
- (Licht et al., 2016) Licht, S., Douglas, A., Ren, J., Carter, R., Lefler, M., Pint, C., 2016, “Carbon Nanotubes Produced from Ambient Carbon Dioxide for Environmentally Sustainable Lithium-Ion and Sodium-Ion Battery Anodes”, *ACS Central Science*, vol 2, no. 3, pp 162–168.
- (Marsh et al., 2006) Marsh, H., Rodríguez-Reinoso, F., “Chapter 9–Production and Reference Material”, in: Marsh, H., Rodríguez-Reinoso, F., *Activated Carbon*, Elsevier.
- (Matesh et al., 2015) Matesh, M., Wang, H., Barrow, C., Yang, W., “Surface Chemistry of Two-Dimensional Layered Nanosheets”, *Nanotubes and Nanosheets*, pp 333–366.
- (Millet & Grigoriev, 2013) Millet, P., Grigoriev, S., 2013, “Chapter 2–Water Electrolysis Technologies”, in: Gandia, L., Arzamendi, G., Diéguez, P., *Renewable Hydrogen Technologies*.
- (Mitsubishi 2006) *Manufacturing Process of Carbon Black*, Mitsubishi Chemical, viewed 12.09.2019.
- (NASA, 1998) *Greenhouse Gases: Refining the Role of Carbon Dioxide*, National Aeronautics and Space Administration, Goddard Institute for Space Studies, viewed 31.07.2019 https://www.giss.nasa.gov/research/briefs/ma_01/

- (Novoselov et al., 2008) Novoselov, K., Blake, P., Katsnelson, M., 2008, “Graphene: Electronic Properties”, in: Buschow J., Flemings, M., Kramer, E., Veysière, P., Cahn, R., Ilschner, B., Mahajan, S., *Encyclopedia of Materials: Science and Technology*, Pergamon.
- (Okwundu et al., 2018) Okwundu, O., Aniekwe, E., Nwanno, C., 2018, “Unlimited potentials of carbon: different structures and uses (a Review”, *Metallurgical and Materials Engineering*”, vol 24, no. 3, pp 145–171.
- (Paragon, 2011) *Paragon Fusion-16 Glass Fusing Kiln*, Paragonweb, viewed 29.12.2019 <https://www.paragonweb.com/Fusion-16.cfm>
- (Peng et al., 2017) Peng, J., Narayana, V., Lau, J. Licht, S., El-Ghazawi, T., 2017, “Thermal Modeling for High Temperature Electrolysis of Lithium Carbonate with Carbon Dioxide Sequestration”, *2017 Ninth Annual IEEE Green Technologies Conference*.
- (Purohit et al., 2014) Purohit, R., Purohit, K., Rana, S., Rana, R., Patel, V., 2014, “Carbon Nanotubes and Their Growth Methods”, *Procedia materials Science*, vol 6, pp 716–728.
- (Qian et al., 2002) Qian D., Wagner GJ., Liu WK., Yu M-F., Ruoff RS, 2002. “Mechanics of Carbon Nanotubes”, *Appl. Mech. Rev.*, vol 55, pp 480–545.
- (Rao et al., 2018) Rao, N., Simha, T., Rao, K., Ravikumar, G., ”Carbon Composites Are Becoming Competitive and Cost Effective”, *Infosys limited*.
- (Reddy et al., 2009) Reddy, B., Gupta, B., Gacche, R., 2009, “An Arsenal for 21st Century Noxious Diseases: Carbon Nanomaterials”, *International Journal of Nanotechnology and Applications*, vol 3, no. 2, pp 61–76.
- (Ren et al., 2015) Ren, J., Li, F., Lau, J., Gonzáles-Urbina, L., Licht, S., 2015, “One-Pot Synthesis of Carbon Nanofibers from CO₂”, *Nano Letters*, vol 15, pp 6142–6148.

- (Scripps, 2019) *The Keeling Curve*, Scripps Institution of Oceanography, viewed 06.08.2019 <https://scripps.ucsd.edu/programs/keelingcurve/>
- (Sitch et al., 2015) Sitch, S., Friedlingstein, P., Gruber, N., Jones, S., Murray-Tortarolo, G., Ahlström, A., et al., 2015, “Recent trends and drivers of regional sources and sinks of carbon dioxide”, *Biosciences*, vol 12, no. 3, pp 653–679.
- (Sridharan & Allen, 2013) Skidharan, K., Allen, T., 2013, “Chapter 12 – Corrosion in Molten Salts”, in: Lantelme, F., Groult, H., *Molten Salts Chemistry From Lab to Applications*, Elsevier.
- (Sunter et al., 2015) Sunter, D., Morrow, W., Cresko, J., Liddell, H., 2015, “The Manufacturing Energy Intensity of Carbon Fiber Reinforced Polymer Composites and Its Effect on Life Cycle Energy Use for Vehicle Door Lightweighting”, *20th International Conference on Composite Materials Copenhagen*.
- (Tepfers, 2008) Tepfers, R., 2008, “Investigation of different types of fibers to strengthen cement paste, mortar and concrete”, *Department of Civil and Environmental Engineering, Chalmers University of Technology*.
- (Warner et al., 2013) Warner, H., Schäffel, F., Bachmatiuk, A., Rümmeli, M., 2013, “Chapter 6– Applications of Graphene”, in: Warner, H., Schäffel, F., Bachmatiuk, A., Rümmeli, M., *Graphene*, Elsevier.
- (WMO, 2016) *COP22 advances global action on climate change*, World Meteorological Organization, viewed 01.08.2019 <https://public.wmo.int/en/resources/meteoworld/cop22-advances-global-action-climate-change>
- (Wu et al., 2017) Wu, H., Li, Z., Ji, D., et al., 2017, “Effect of molten carbonate composition on the generation of carbon material”, *RSC Advances*, 7, pp 8467–8473.

(Yu et al., 2017)

Yu, Y., Li, Z., Zhang, W., Li, W., Ji, D., Liu, Y., He, Z., Wu, H., 2017, "Effect of BaCO₃ addition on the CO₂-derived carbon deposition in molten carbonates electrolyzer", *Royal Society of Chemistry*, vol 42, pp 1208–1215.