

Conversion of Carbon Dioxide Gas to Hydrocarbon Fuels by Electrolysis in Molten Salts

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Abstract

Using fossil fuels in power generation has not been considered a serious issue until recent justification of the depletion of fossil resources in addition to the rising atmospheric temperature as a result of increasing CO₂ emission from fossil fuel consumption. Technologies that can absorb CO₂ from the emissions and, more substantially, convert CO₂ economically into useful products, e.g. materials or fuels, with lower carbon intensity are urgently needed and more desirable than simply storing the gas underground. Performing such conversion at high temperatures (200-600 °C) can offer both thermodynamic and kinetic advantages. Molten salts are ideal media for high temperature reactions but their use for the conversion of CO₂ and H₂O to beneficial products has not yet been examined properly. Thus, this research aims to investigate the feasibility of producing hydrocarbons by the electrochemical reduction of CO₂ and H₂O (steam) in molten salts at the atmospheric pressure.

Two different mechanisms were suggested in literature for hydrocarbon formation after the co-electrolysis of CO₂ and H₂O to CO or C (carbon) and H₂ in molten salts. The first one is the partial oxidation of CH₄ that is produced feasibly in molten salts (e.g. $C + 2H_2 = CH_4$). Due to the sufficient availability of oxide ions (O²⁻) in molten salts, where the partially reduced species of oxygen (O₂⁻, O₂²⁻) are obtained, the produced CH₄ can be transferred to C₂ and other hydrocarbons by the catalytic oxidative coupling in liquid phase. However, there is a possibility of CH₄ reaction with O₂ to CO₂ and H₂O. The second mechanism is the direct reaction of carbon with atomic hydrogen adsorbed primarily on the cathode producing different hydrocarbons. However, some other studies detected CH₄ attached with slight amounts of long-chain

hydrocarbons in the cathodic gas product during the direct electrolysis of molten carbonates mixed with hydroxides.

The electrolyser used in this work resembled that for CO₂ reduction to CO in lithium containing molten carbonates at 900 °C using a cell with partitioned cathode and anode compartments. However, in addition to the ternary molten carbonates (Li₂CO₃-Na₂CO₃-K₂CO₃) of (43.5:31.5:25 mol%), this work also studied the molten chloride salts of KCl-LiCl of (41:59 mol%) and molten hydroxides of LiOH-NaOH (27:73 mol%) and KOH-NaOH (50:50 mol%). The electrolyser was employed at different temperatures (220-600 °C) depending on the molten salt applied. Various cathodic gases were produced during the electrolysis as confirmed by gas chromatography.

At the specified temperatures in this work, olefin hydrocarbon species between (C₂-C₅) rather than paraffins were found (as the reaction of CO with H₂ is feasible) by a total production rate of 0.06 mmol/h of the whole product associated with H₂ and CO in molten carbonate electrolysis at 1.5 V and 425 °C under a feed gas of 15.6 molar ratio of CO₂/H₂O. The priority of olefin formation can be confirmed also by the mechanism of partial oxidation of CH₄. The summation of current efficiencies for different cathodic products was close to 100%. The CH₄ gas was the predominant hydrocarbon fuel produced during the electrolysis in molten hydroxide in general. No significant indication of hydrocarbon formation was found in the molten chlorides from CO₂ reduction or conversion even at 1.3 bar of CO₂.

The effect of the molten salt temperature, applied electrolysis voltage and the CO₂/H₂O ratio of the feed gas were also examined during the electrolysis in molten carbonates and hydroxides. By increasing the electrolysis temperature from 425 °C to 500 °C, the number of carbon atoms in the hydrocarbon species produced in the cathodic gas rose to 7 (C₇H₁₆) with a production rate of 1.5 μmol/cm².h at a CO₂/H₂O ratio of 9.2 increasing the average molecular weight

of the product and thus the calorific value. However, the hydrocarbon fuel content in the cathodic gas product in general was found to be higher in the case of high inlet gas CO₂ content (CO₂/H₂O=15.6) by 18% at 425 °C and 41% 500 °C which can be considered as the optimum condition for hydrocarbon formation in this research. Due to the prospective carbon formation, the electrolysis to produce hydrocarbon in molten carbonates was more feasible at 1.5 V than that performed at 2 V. In molten hydroxide case, the CH₄ production rate increased when the applied voltage was increased from 2.0 to 3.0 V despite the reduced current efficiencies.

Because the electrolytic conversion can be very fast and achieved without using any catalyst, such as the precious metals used in other CO₂ reduction routes in water, the results reported in this thesis are promising and encouraging for further fundamental investigation and technological development.

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Chapter 1

Introduction

1.1 Research motivation

Over the past few decades, two major issues have captured the attention of both scientists and policy makers: global warming due to the increasing levels of carbon dioxide gas (CO₂) in the atmosphere, and the rapid depletion of fossil fuels as an energy resource. Regarding the latter, the consumption of fossil fuels is still very large and oil reserves are expected to be yet exploited over the next 50 years (Abbott 2010). In addition, fossil fuels are non-renewable because they have been formed over millions of years and cannot be reproduced overnight using conventional industrial applications.

To tackle these complications, two solutions have been proposed. The first method is by using renewable energy resources such as wind, solar, nuclear or geothermal energies to avoid and reduce the emissions of greenhouse gases up to acceptable limits. The use of these sources as alternatives for high CO₂ emitting power sources can be summarised as follows:

Nuclear energy

Nuclear energy is a convenient form of energy. Nuclear power is currently able to supply more than 16% of total world electricity (World Energy Council 2001). However, besides safety and other non-proliferation aspects, the greatest concern with nuclear power is still the safe disposal of spent fuel (containing uranium) from the reactor. Some technologies have been proposed however (such as molten salt electrolysis) to reprocess the spent

fuel, thereby extracting useful metal oxides from the nuclear reactor (Stevenson, Hu et al. 2014). Yet, this route is still complicated due to the large amount of radioactive waste from the reprocessing plant.

Geothermal technology

This kind of energy can be obtained from the natural heat of the earth. The hot rocks in the earth's interior can be artificially fractured and water will be forced in circulation between injection and producer wells.

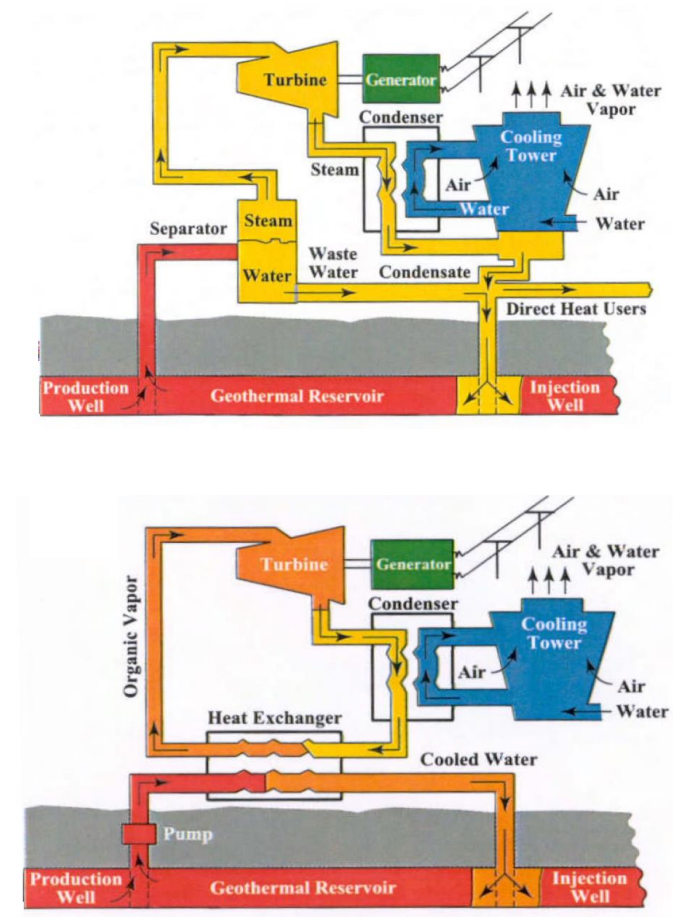


Figure 1.1. A schematic diagram of the geothermal energy plant (a) generating superheating steam (b) heating another fluid to operate the turbine. (World Energy Council 2001)

The hot water or steam produced can operate a turbine directly (generating electricity) or heat a secondary working fluid (isobutene for example) to force the turbine's rotation post evaporation as shown in Figure 1.1.

However, feasible access to hot rocks that are essential for producing water at sufficiently high temperatures for electricity generation, is yet to be provided for a vast number of countries. Moreover, the long-term prospects of this technology depends on the economic viability of the hot rocks themselves (World Energy Council 2001).

Wind and solar energy.

These two kinds of renewable energy play a significant role in electric power generation nowadays. They are non-polluting and inexhaustible, non-fossil fuel based, renewable energy resources but are still affected by intermittency based on the prevailing weather conditions. Nevertheless for solar energy in particular, it is estimated that every hour the earth receives sufficient solar energy to cover the entire world's energy requirement for a year (World Energy Council 2001). Moreover, the Department of Energy (DoE) USA has predicted that if the solar irradiance of 1% of the earth's surface is converted with 10% efficiency into storable energy, it would provide a source that can cover several times the energy requirements of the world by 2050 (Ganesh 2014).

All of the above renewable energies do not involve CO₂ sequestration through their electricity generation. To tackle CO₂ emissions efficiently, it would be preferable if some of the renewable energy resources were introduced into an existing energy infrastructure (power system) as a "drop-in" form of energy. Examples of this can include the synthesis of fuels from CO₂ or fertilizers from CO₂ and biomass as will be discussed later.

In this review of suitable renewable energy resources to address intensive carbon footprint energy types, two groups of fuels are mentioned that can be synthesised utilising renewable energy: biofuels and fuels derived from CO₂ and renewable energy.

1.1.1 Biofuels

During photosynthesis, biomass absorbs natural solar energy to capture CO₂ from the atmosphere. Therefore, no additional renewable energy needs to be provided for the above process. Additionally, no renewable energy is needed (as claimed) to convert the biomass into the various kinds of biofuels such as biogas, liquid biofuels, etc. The carbon-rich products that can be obtained from biomass can be seen in Figure 1.2. The major problems associated with biomass can be classified as follows:

- The input energy (embedded indirect carbon emissions) required to cultivate biomass must be minimised. Therefore, the utilisation of low-input energy and high diversity, grassland biomass should be expanded rather than crop based biomass (Zhou, Xiao et al. 2009) .
- N₂O (as another kind of greenhouse gas) emissions from agriculture soil can be increased because the cultivation of biomass is enhanced intensively with N-fertilizers (Crutzen, Mosier et al. 2008). This issue can be solved by reducing the use of N-synthesis fertilisers and introducing waste organic fertilizers instead as soil fertilization is essential for developing renewable bioenergy technologies.

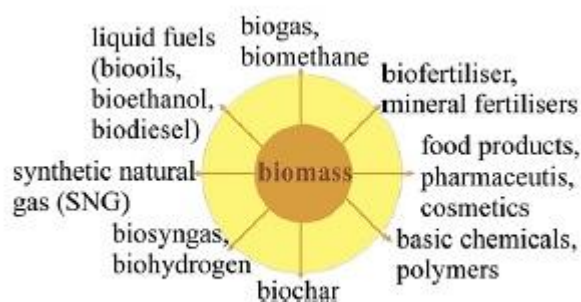


Figure 1.2. Carbon-rich products obtained from biomass (Budzianowski 2012a).

For a brief explanation, two of the bio-energetic technologies that have been mentioned in Figure 1.2 for achieving a low carbon footprint, will be illustrated in this section:

1. Biogas

Biogas including CO_2 and CH_4 produced from the anaerobic digestion of biomass through biological routes, can be upgraded to bio-methane through the separation of CO_2 (Avcioglu and Türker 2012). Methane gas itself can be described as a high-heat value gas with low carbon intensity (compared to other synthesis gases) and can be introduced thus directly into a natural gas grid. Alternately, flue gases that are produced from biogas combustion are very rich in CO_2 (~50%) compared with flue gases from coal or fossil fuel combustion which contain only 15% of CO_2 (Budzianowski 2012b). The CO_2 -rich gases can then reduce the cost for CO_2 capture in general due to higher driving forces for CO_2 separation.

If the produced CO_2 is captured and recycled through anaerobic digestion (AD) units, its concentration after the conversion of biomass carbon during the

digestive process, will be minimised. Microorganisms will still synthesise CH_4 under CO_2 enriched gas conditions (Budzianowski 2010a).

Furthermore, biogas can be converted to CO , CO_2 and H_2 through the oxy-reforming fuel cell cycle (ORFC) as shown in Figure 1.3. Hydrogen gas can be separated accordingly from CO_2 (by one of the methods to be explained later) and enters the fuel cell, thereby producing electricity. The former separation technique is more feasible than the separation of CO_2 - N_2 or CO_2 - CH_4 mixtures due to the various separation properties of H_2 and CO_2 (such as high pressure adsorption or membrane) (Budzianowski 2010b). The objective of the ORFC is then to decompose CH_4 into purely H_2 and CO_2 as CO will be simultaneously oxidised entirely to CO_2 . The oxy-reforming operation can be summarised as CH_4 being split to CO and H_2 by the reaction of CH_4 with CO_2 in the oxygen-steam environment. CO is then oxidised to CO_2 , thereby providing energy for the aforementioned reaction (CH_4 to CO and H_2) and for H_2O splitting as both of these reactions are endothermic. To avoid the dilution of products with N_2 gas, pure O_2 was used as an oxidiser with the remaining CO being fully oxidised to CO_2 .

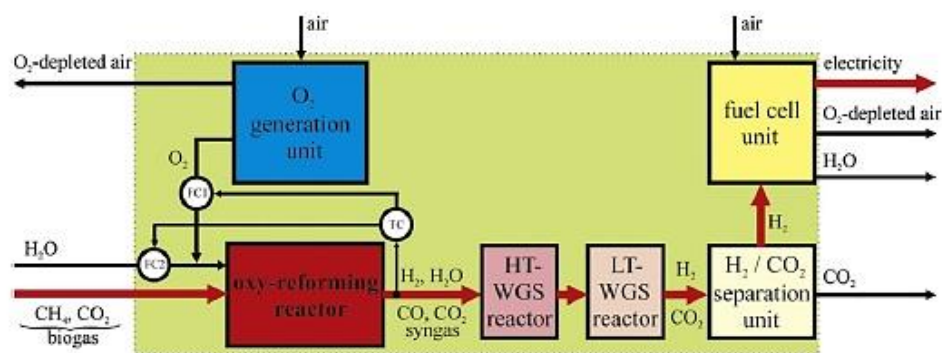


Figure 1.3. Diagram of the biogas utilised in the oxy-reforming fuel cell cycle (ORFC) (Budzianowski 2012b).

The ORFC process allocates for the auto-thermal conversion of biogas into gas including almost 68% H₂ and 32% CO₂. CO₂ gas is then suitable for either CCS (Carbon Capture and Storage) or CCR (Carbon Capture and Recycling).

2. Liquid biofuels and biochar.

Liquid and biochar fuels can be produced from biomass without releasing CO₂ in contrast with the case of biogas generation. Biomass is converted by pyrolysis (for instance) to biochar and liquid biofuels. Biochar is described as a carbon-rich charcoal that can be used as an effective soil fertiliser and a unique storage mechanism for the carbon found in soil. This is a promising characteristic for CO₂ sequestration (Figure 1.4) (Woolf, Amonette et al. 2010). The Life Cycle Assessment (LCA) (which is the environmental impact of the biochar product) estimates that net greenhouse gas emissions can be reduced by 850 kg CO₂ equivalent per tonne of the dry feedstock charcoal due to this process (Roberts, Gloy et al. 2010).

On the other hand, bioethanol produced from the fermentation of cellulosic biomass (such as switchgrass or forest residues) at low-temperatures can contribute also to reduced carbon emissions as it comprises of lower indirect energy consumption than corn-based bioethanol for instance (Oladosu 2012). Such processes like cellulose-bioethanol formation are still costly and under development because they require cellulose pre-treatment to increase the enzyme accessibility for better cellulose digestibility (Alvira, Tomás-Pejó et al. 2010).

Also, biofuels can be produced from bio-syngas derived from biomass gasification (Seggiani, Vitolo et al. 2012). These kinds of fuels are high in carbon-rich products with less CO₂ emissions from the power cycle. The

energy efficiency of woody biomass conversion (for instance) to bio-syngas, can be 70-72% (Seiler, Hohwiller et al. 2010). However, the cost of biomethanol, bioammonia and biodimethylether (DME) for example produced from syngas derived from forest residues, is still higher than the cost of their fossil fuels-derived counterparts.

Therefore in summary, prior to using biomass to extract CO₂ from the atmosphere as a solution for CO₂ mitigation, the following proceedings should be ensured:

1. The derived biomass from green plants must require little cultivation (fuel and fertilizers).
2. The conversion of biomass to biofuel demands very little input energy (drop-in energy).
3. CO₂ produced from the conversion is captured in a low cost and feasible way, and then sequestered also in a practical manner.

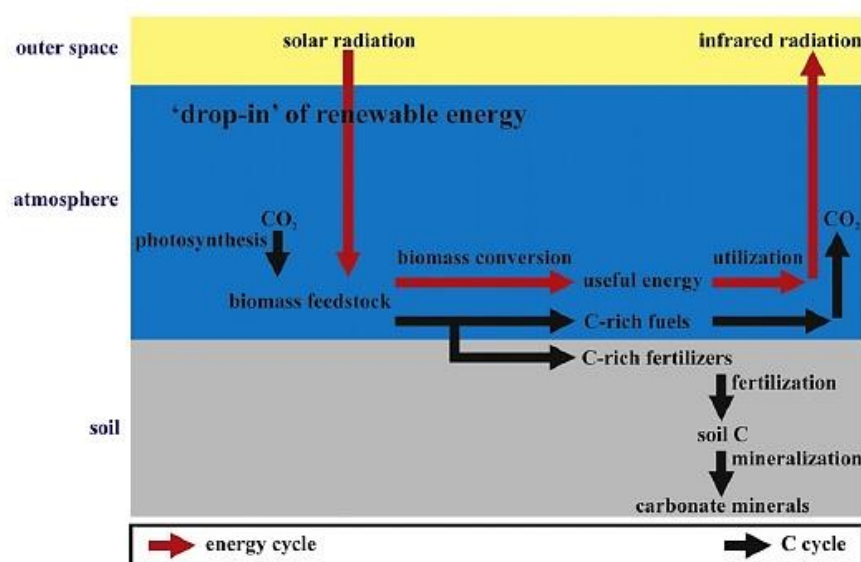


Figure 1.4. The energy and carbon cycle for C negative biofuels (Budzianowski 2012b).

1.1.2 Fuels derived from CO₂ and renewable energy

The carbon (C) intensity of energy is usually linked to the primary or useful energy obtained in power generation. For instance, the C intensity of the primary energy obtained from high grade coal is about $2.8 \times 10^{-5} \text{ g C J}^{-1}$ (Budzianowski 2012b). After considering the electricity-to-coal low efficiency ratio, C intensity of the useful energy for this fuel can be as high as $7 \times 10^{-5} \text{ gC J}^{-1}$. Alternately, the intensity of primary energy obtained from high methane content natural gas is 1.35 g C J^{-1} . Therefore, the higher the calorific heat with appropriate carbon content fuel employed in power generation, the lower the C intensity that is obtained. For instance, C₂H₆ displays lower C intensity than C₂H₄ as the former produces more H₂O moles during combustion with higher heat. Furthermore, generating C-rich fuels from CO₂ produced in turn from low-grade fuels (high C intensity) will be a suitable method for CO₂ reduction in totality.

On the other hand, renewable energy resources are often unstable and require an energy storage facility system such as the case for solar panels and wind turbines. CO₂ capture and conversion (CCC) is therefore a suitable technology to store renewable energy in the form of hydrocarbon fuels or C-rich energy carriers. This is particularly the case for molten salt mediums where electrolysis can be carried out in the event of energy intermittency if the energy requirement for electrolysis itself, is minimised as the salt will remain liquid for a while. At the same time, the CCC will enhance the net removal of CO₂ from the atmosphere. Carbon capture and conversion may need the addition (or drop-in) of renewable energy as a zero intensive carbon source in different ways.

In CO₂ hydrogenation to methanol for example, the reaction needs thermal

energy first for CO₂ separation from flue gases (by reactive absorption), followed by renewable H₂-CO₂ hydrogenation, compression work in the high pressure methanol synthesis reactor and finally thermal energy for methanol separation (by distillation) (Budzianowski 2012b).

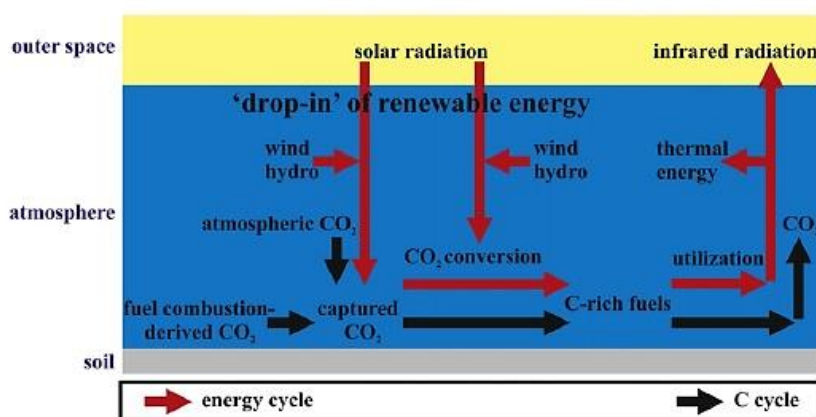


Figure 1.5. Energy and carbon cycles in C negative fuels derived from CO₂ and renewable energy.

Figure 1.5 explains how C negative fuels can be derived from CO₂ and renewable energy. It displays the energy cycle and the carbon cycle. From the energy cycle, a part of the infrared released energy into space can be retained as thermal energy and compensates the energy taken from the environment by renewable technologies such as wind or hydro. However, many CO₂ conversion processes appear not entirely economical these days. As CO₂ is a very stable molecule, the aforementioned processes require a lot of energy.

Using solar or excess nuclear energy to convert CO₂ gas into carbon monoxide (CO) or water to hydrogen (H₂) gases by thermochemical reactions at

elevated temperatures (over 1000 °C), can be a useful route for CO₂ and H₂O dissociation. However for such approaches under severe conditions, hydrocarbon fuels will not be formed directly i.e. in one stage. In addition, these processes need to alternate between heating and cooling to transfer the required heat as most of these reactions are endothermic in nature (Ao, Wang et al. (2008)).

In this study, a new process that is capable of the co-reduction of CO₂ and H₂O to hydrocarbon species is demonstrated by electrolysis in molten salts at temperatures far below 1000 °C. This process can be done in one cell and the products will be released separately in the anode and cathode compartments.

1.2 Carbon capture technologies

There are three technologies for carbon dioxide capture from flue gas streams: post-combustion; pre-combustion and oxyfuel combustion (Olajire 2010) as shown in Figure 1.6.

In the post-combustion process, fuel is combusted normally with air and the released flue gas contains 4-14% CO₂. To separate this low concentration CO₂, very large equipment is required, adding immensely to the already high capital costs. Moreover, powerful chemical solvents should be used in this event to absorb the lower contents of CO₂ in the flue gas (Mangalapally, Notz et al. 2009).

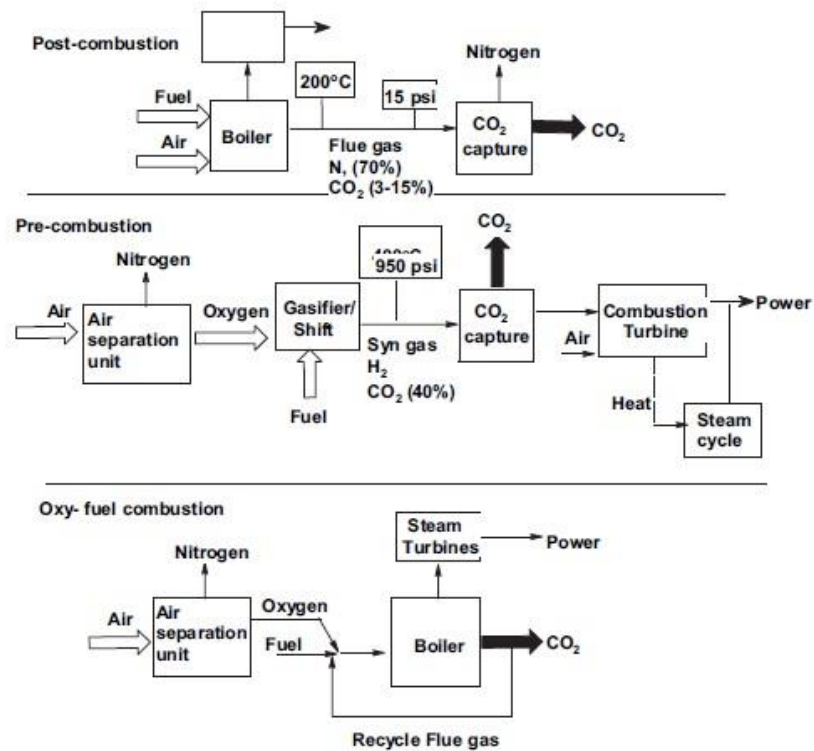


Figure 1.6. Block diagrams showing post-combustion, pre-combustion and oxyfuel combustion techniques (Olajire 2010).

In the pre-combustion process, fuel is gasified, partially oxidised (with air or oxygen) or reformed with steam producing mainly CO and H₂. The products then undergo a first shift reaction with a catalyst to produce more CO₂ with H₂ as shown below:





The resulting CO_2 here is in higher concentration in comparison to the post-combustion process and it can be separated easily from H_2 using more appropriate methods. The total capital cost of such type of a generating facility are still unfortunately very high (Pires, Martins et al. 2011).

In the oxyfuel combustion process, fuel will be combusted with pure oxygen instead of air. Due to this, the flame temperature is quite high. Therefore, some of the produced CO_2 can be recycled through the feed to reduce the flame temperature; this is similar to the process occurring in a normal air blown combustor (Olajire 2010). The advantage of oxyfuel combustion is that the fuel gas has a CO_2 content of over 80% and thus only simple purification is required. Also, NO_x gas emissions are suppressed. Moreover, there is no need for a chemical separation process for oxygen production and CO_2 capture, thereby avoiding the use of any reagent and/or solvent and reducing the operating costs and the environmental disposal of the related solid or liquid waste. The main disadvantage though is that a high quantity of O_2 gas is required, raising both the capital cost and the energy requirement.

1.3 Carbon capture methods

Several technologies can be employed for CO_2 separation from the flue gases. These processes vary from each other in terms of the cost and feasibility of CO_2 production:

1.3.1 Absorption

Absorption is a common process in the industry and it is used among other

methods particularly in the treatment of acid gases such as H_2S , NO_x and CO_2 . Alkanoamine solvents are usually used for the perfect absorption of CO_2 in the industry (Mangalapally, Notz et al. 2009). However, the inlet flue gas that flows to the absorber needs to be cooled prior to being in contact with the solvent. Moreover, there are some obstacles in this process. Firstly, the cyclic loading capacity of CO_2 in the solvent is limited (Lee, Maken et al. 2008). Secondly, the regeneration process consumes relatively high energy (3.7 GJ/ton- CO_2) (Pires, Martins et al. 2011). Also, there will be a significant loss of the solvent by evaporation (1.4 Kg/ton- CO_2). And finally, in addition to the promotion of equipment corrosion, the solvent itself undergoes degradation due to the effect of oxygen-rich fuel gases. Alternate methods for CO_2 absorption employ CO_2 chemical interaction such as the carbonation of CaO to capture CO_2 from flue gas at high temperatures (around 700 °C) (Alonso, Rodriguez et al. 2011).

1.3.2 Adsorption

Adsorption is also a proper process for CO_2 capture. CO_2 molecules, even in small quantities in the inlet stream, can adhere to (adsorbed) on a solid material (adsorbent) in a selective manner. Compared to absorption, adsorption offers lower energy requirements (Drage, Smith et al. 2009). Two methods can be employed to successfully transition between the adsorption and desorption steps in a cyclic operation: by changing the pressure (pressure swing adsorption (Reynolds, Ebner et al. 2006)) or the temperature (Thermal swing adsorption (Sjostrom and Krutka 2010)). However, the flue gases still need to be cold and dry in addition to the removal of poisonous substances such as SOO_x (SO_2 , SO_3) prior to the introduction to the adsorption site.

Also, two parameters are important and need to be taken into account: spent

time of regeneration and the adsorbent lifetime.

1.3.3 Gas separation membranes

The gas permeating process was basically explored as a low cost technology for the separation of CO₂ and N₂ in the flue gas using membranes with significant CO₂ permeation and selectivity, particularly when a high level of purity of the gas product (CO₂) is not required (Powell and Qiao 2006). Polymeric membranes are preferred due to their low cost and high mechanical stability. However, the treatment of enormous quantities of flue gases emitted from a power station requires a very large membrane area, thereby increasing the total cost of the technology (Favre 2007). Moreover, the process embeds high energy requirements for gas compression and needs cooling of flue gases. This is because the high temperature inlet gas can rapidly destroy the membrane. Water and SO_x contamination can also reduce CO₂-recovery through the competitive adsorption and plasticisation of the polymer itself (Scholes, Kentish et al. 2009).

1.3.4 Cryogenic distillation

Cryogenic distillation is an air separation process which is basically designed to separate N₂ from O₂ by gas condensation due to the difference in boiling points. The oxygen gas for instance can then be introduced to the oxyfuel combustion process as mentioned previously in the overall combustion process. Cryogenic technology can capture CO₂ in a liquid form (at high pressures) that will be suitable for CO₂ storage and usable for enhanced oil recovery (for instance) (ZareNezhad and Hosseinpour 2009). The last outcome can be compared with the other previous applied technologies of CO₂ capture as they too deliver the final output gas at atmospheric pressure. The water content in flue gas is also a significant issue and should be minimised

in this process to prevent the plugging by ice or the rapid change in pressure drop during the operation.

1.3.5 Carbon dioxide storage.

Carbon capture and storage can be a possible way to address gas emissions. In this process, CO₂ will be captured, compressed and stored underground away from the atmosphere for an extended period of time.

Regardless of the energy required to bury CO₂, the moot point relates to sequestration leakage and its effect on the environment. Storage of gas in the ocean is considered to be the largest sink of CO₂ (Khoo and Tan 2006). However, due to the effect of CO₂ on marine life, geological sequestration (e.g. oil and gas reservoirs) is preferably the viable option (Celia and Nordbotten 2009). The reservoir should have a satisfactory sealing caprock to be adequate for the integrity of storage site (Pires, Martins et al. 2011).

In general, the capture of CO₂ contributes to almost 75% of the whole cost of the CCS-route and the production costs of electricity will increase by over 50% (Feron and Hendriks 2005) as shown in Figure 1.7.

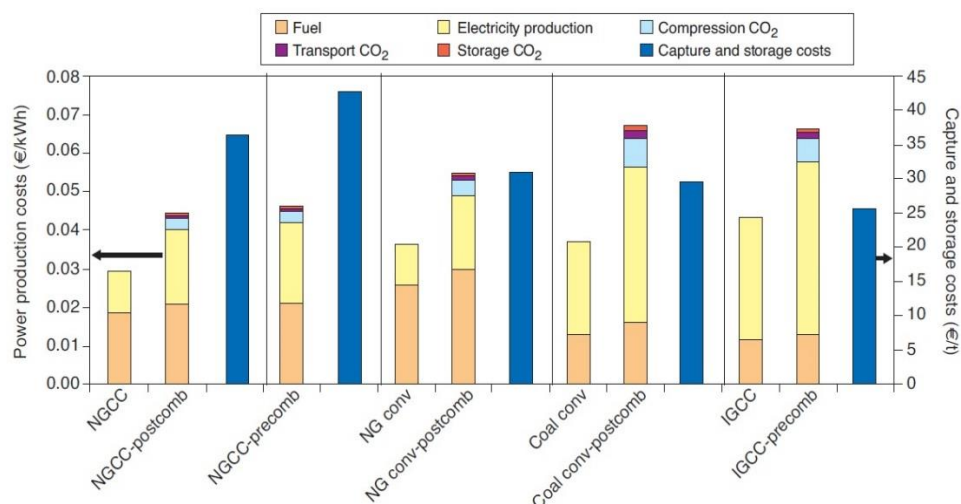


Figure 1.7. Electricity production cost for various technologies. (Feron and Hendriks 2005)

The abbreviations for electricity production technologies with or without carbon capture shown in Figure 1.7, are listed in Table 1.1.

Table 1.1. Electricity production technologies in Figure 1.7.

Abbreviation	Electricity Production technology
NGCC	Natural gas-fired combined cycle
NGCC-postcomb	including post-combustion CO ₂ capture
NGCC-precomb	including pre-combustion CO ₂ capture
NG conv	Natural gas-fired conventional (boiler) power plant
NG conv-postcomb	including post-combustion CO ₂ capture
Coal conv	Coal-fired conventional (boiler) power plant
Coal conv-postcomb	including post-combustion CO ₂ capture
IGCC	Integrated coal-gasifier combined cycle
IGCC-precomb	including pre-combustion CO ₂ capture

1.4 Electro-reduction of CO₂ into materials and fuels at low temperatures.

Co-electrolysis of CO₂ and water can be performed at low temperatures (<100 °C) using an aqueous solution to recycle CO₂ to CO or some hydrocarbon species instead (e.g. CH₄, C₂H₄, C₂H₆ etc.) (Hori, Murata et al. 1989). Many process parameters will affect the process such as the electrode material, temperature, pressure, pH value, catalyst, potential and the appropriate electrolyte itself. Significant research has gone into finding a suitable catalyst for this conversion process in order to reduce energy consumption, improve reaction kinetics and increase product selectivity. Nevertheless, the amount of hydrocarbon gas from the electrolysis is very low due to the poor solubility of CO₂ inside the aqueous medium and the proximity of the electro-reduction potential of both water and CO₂ (H⁺/H₂O potential is -0.41 V vs Normal Hydrogen Electrode, NHE, whereas CO/CO₂ potential is -0.52 V vs NHE at pH=7). So, hydrogen generation will be preferred thermodynamically over CO₂ reduction.

Regarding using hydrogen gas as a future fuel, it is worth mentioning that the gas requires a high amount of energy during its formation in general and has low volumetric energy compared with liquid hydrocarbon fuels as seen in Table 1.2. Although H₂ gas has a high energy content on a mass basis in contrast, it produces no CO₂ during combustion whereas some of the hydrogen production techniques (such as steam reforming) result in higher greenhouse emissions than those for gasoline production as an example.

On the other hand, CO₂ electro-reduction can occur in liquid alcohol e.g. methanol, and the products are almost the same as in an aqueous solution.

Table 1.2: Energy densities of some energy carriers on a mass and volume basis (lower heating value LHV) (Gattrell, Gupta et al. 2007).

Fuel	Volumetric energy density (kJ/L or MJ/m ³)	Mass energy density (MJ/kg)
Diesel fuel	35,760	42.9
Bio-diesel	32,580	41.5
Gasoline	32,020	43
LPG (liquefied petroleum gas) (mostly propane)	23,500	46.4
Ethanol	21,200	27
Methanol	15,800	20
207 bar NG (3000 psi natural gas) (mostly methane)	9900	74
207 bar H ₂ (3000 psi)	1810	120

The supporting electrolyte, types of electrode material and catalyst are all important here. The current efficiencies of these processes and other techniques will be discussed in the next chapter.

1.5 Electro-reduction of CO₂ into materials and fuels at high temperatures.

Increasing the electrolysis temperature (200-900 °C) will reduce the need for more expensive catalytic materials due to faster reaction kinetics leading to lower capital costs (Graves, Ebbesen et al. 2011). However, some catalytic metals can still be used as a cathode or anode material depending on the condition of the electrolyte to enhance the performance of the cell towards hydrocarbon production.

Using high temperature electrolysis between 800 and 1000 °C with solid oxide electrolytes for instance, will exhibit both thermodynamic and kinetic advantages throughout the reduction of both CO₂ and H₂O. Also, because of the high temperature medium, a lower amount of electrical energy is required. Two types of cells can be used for high temperature electrolysis: those with molten salt electrolytes and those with solid oxides.

In the solid oxide electrolysis cells (SOEC), CO₂ or/and H₂O can be reduced generally at temperatures higher than 800 °C to produce synthesis gas which is a mixture of H₂ and CO.

The cathode and anode reactions in a solid oxide electrolysis cell (SOEC) are summarized below.



Or/and



So, the overall reaction will be:



There are four species (CO₂, H₂O, H₂ and CO) produced on the cathode and oxygen gas is evolved at the anode. Further hydrocarbons can be obtained finally from the synthesis gas by Fischer-Tropsch synthesis at a lower temperature stage (Becker, Braun et al. 2012). Due to high temperature conditions, CO or H₂ may also be produced from the forward or reverse water gas shift reaction (RWGS) (reaction 1.5).

Molten salts basically exhibit the same chemistry regarding CO_2 and H_2O reduction as in solid oxide electrolysis except that CO_2 can be also reduced to carbon in addition to carbon monoxide depending on the operating conditions; this can thereby affect the process. Deposited carbon on the cathode can facilitate the formation of different kinds of hydrocarbons (rather than CO) by reacting with hydrogen gas produced via water reduction on the metal cathode surface itself.

Molten salts are preferred over solid oxides regarding CO_2 reduction for a variety of reasons. Besides a wide electrochemical window, high electric conductivity, relatively low cost and their reactivity with CO_2 , the possibility of carbon or CO hydrogenation after electrolysis in molten salts is much more significant. Molten salts therefore can be employed to convert CO_2 electrochemically to hydrocarbon gas or liquid fuels using renewable energy (Chery, Albin et al. 2014).

The key point here is that the electricity used to convert CO_2 must be both renewable in nature and low cost. Alternately, the conversion process will reduce less CO_2 than initially released in terms of producing electricity for the process.

1.6 Research aim and objectives

The main aim of this research is to investigate the feasibility of reducing carbon dioxide gas (CO_2) and steam (H_2O) by molten salt electrolysis for hydrocarbon fuel production. To achieve this aim, the research was carried out with the following objectives;

- Design and fabrication of a high temperature molten salt lab reactor and electrodes for the purpose of performing electrolysis.
- Selection of the appropriate molten salts for the electrolysis of H₂O and CO₂.
- Investigation of hydrocarbon formation through molten salt electrolysis using gas chromatographic analysis.
- Effects of process variables such as voltage, electrode material, CO₂ to water ratio, molten salt temperature on the electrochemical process.

1.7 Scope of thesis.

Chapter 1 explains the research motivation and outlines the different techniques for CO₂ electro-reduction at both low and high temperatures. It also introduces the research aim and objectives, including the overall scope of the thesis.

A background on previous studies on CO₂ recycling to fuels in general is introduced in Chapter 2. Subsequently, the chapter explains the techniques for CO₂ and H₂O co-electrolysis in particular at low and high temperatures by a number of researchers and the justification of hydrocarbon formation in the case of molten salt applications. The prospect for generating hydrocarbon species during electrolysis in molten salts is also reviewed. The effect of temperature, applied voltage and CO₂ content in the feed gas for molten salt electrolysis is also reviewed.

Chapter 3 starts with the introduction of the equipment and chemicals that were used to conduct the experimental work. The design and arrangement of a molten salt electrolyser that was employed to perform the research is

included. This chapter outlines also analytical techniques like gas chromatography for the analysis of hydrocarbon gas products.

The configuration of a new reactor for CO₂ and H₂O co-electrolysis is justified and tested primarily in Chapter 4 based on some of the previous applications for the purpose of hydrocarbon production.

The particular test of the last reactor is outlined in Chapter 5 using three different mixtures of molten salts. The justification of specific hydrocarbon formation is discussed in each category of molten salts.

Chapter 6 illustrates the influence of process variables including temperature, applied voltage and CO₂/H₂O ratio in the feed gas on the co-electrolysis of CO₂ and H₂O themselves in the above mentioned molten salts in addition to the likely effect on hydrocarbon production.

The explanation for the optimum conditions of hydrocarbon production in the molten salt electrolyser are presented in Chapter 7. The results are optimised based on the production rates of generated fuels in general and hydrocarbons particularly. The conclusions of this research and recommendations for future work are provided in Chapter 8.

Chapter 2

Literature review

The recycling of CO₂ gas (with or without H₂O) into valuable materials has been studied by many researchers who have put forth various process techniques for this purpose. The formation of hydrocarbon fuels though is demonstrated in some of these processes by different interpretations. This chapter therefore compares available literature describing the mechanisms applied for CO₂ and H₂O dissociation in each process and the proposed justification for hydrocarbon fuel evolution. In particular, the mechanism of hydrocarbon formation in molten salts via electrolysis is addressed separately. The effect of process variables such as salt composition, temperature and applied voltage is also discussed.

The dissociation of CO₂ or H₂O molecules to CO and H₂ respectively (for instance) requires a high energy of conversion due to the lower potential energy levels of CO₂ and H₂O as shown in Figure 2.1, taking into consideration their Gibbs' energies of formation as follows:



Where $\Delta_f G_{298}$ for CO₂ and H₂O are -394.3 and -228.6 KJ/mol respectively. Therefore, because of the lowest Gibbs energy levels for the formation of CO₂ and H₂O molecules, a minimum amount of electric energy must be introduced to drive the CO₂ and H₂O conversion (reactions 2.1 and 2.2 for instance) as shown in Figure 2.2.

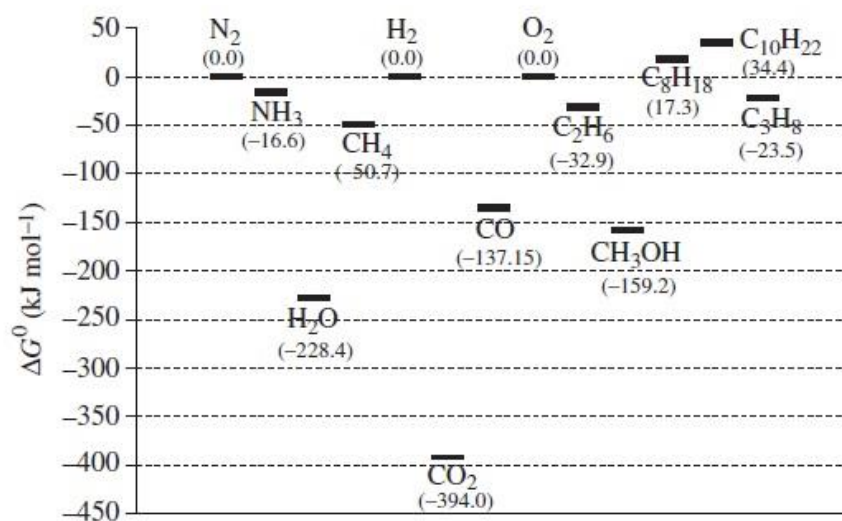


Figure 2.1. $\Delta_r G_{298}$ for selected chemicals (data compiled and calculated from JANAF-NIST database). (Chase 1998; Jiang, Xiao et al. 2010)

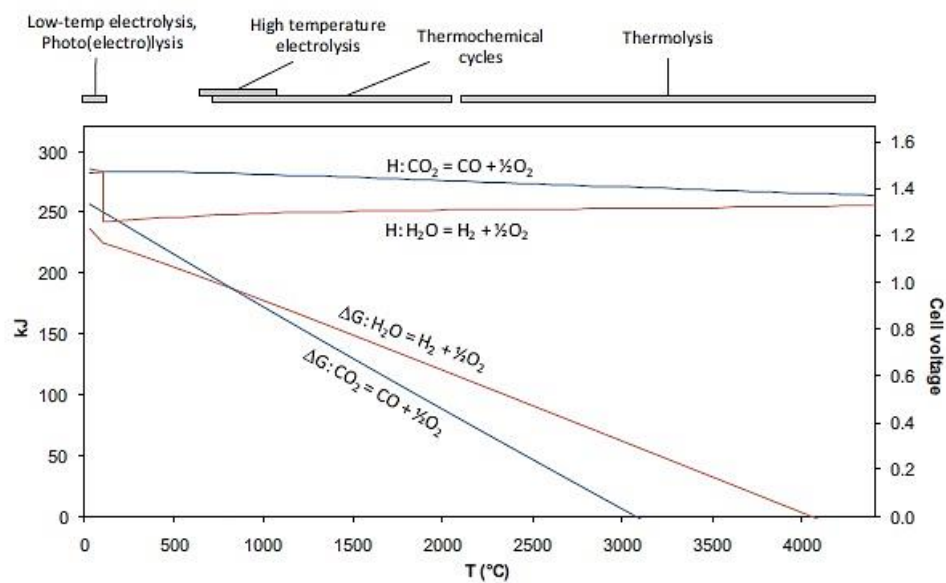


Figure 2.2. Thermodynamics of CO₂ and H₂O conversion to CO and H₂. The electrochemical cell potential (voltage) corresponding to energy input is on the right hand side. The upper two plots represent the ΔH alteration versus temperature (Graves, Ebbesen et al. 2011).

However, CO₂ conversion in particular can be performed with no need for any external energy if a co-reactant with a high energy level is involved as shown in Figure 2.3. The co-reactant (such as H₂, alkenes and amines) will provide the required energy to proceed with the conversion catalytically at moderate temperatures (Figure 2.3).

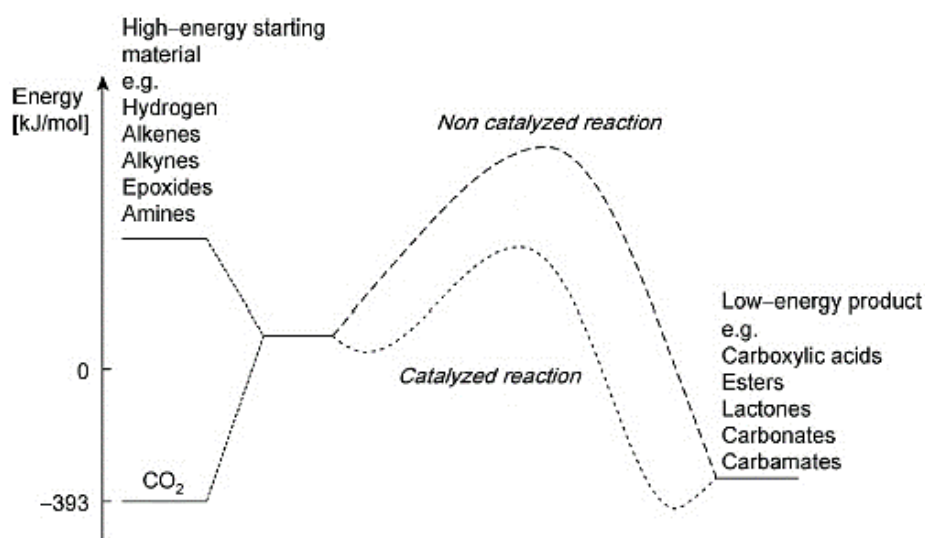


Figure 2.3. Energy levels of CO₂, high energy reactant and low energy products (Alper and Yuksel Orhan 2017).

The formation of a specific kind of hydrocarbon is normally controlled by kinetic factors (by the catalyst being selective in favouring one reaction path of the desired product over the others as by products). Some fuels like alcohols or CH₃OH in particular (Figure 2.1) seem thermodynamically more feasible to be formed than other kinds of hydrocarbons (such as CH₄, C₂H₆, and C₃H₈) as shown in Figure 2.1.

Nevertheless, CO₂ and H₂O can be reduced directly to CO, H₂ or hydrocarbon species such as HCOH, CH₄ and C₂H₄ (as will be illustrated later in more detail) expending a significant amount of external energy. For instance, the energy required to drive the last two reactions (2.1,2.2) at low temperatures (<1000 °C) should be provided by electricity in order to cover the differences in Gibbs energy according to the following equation (Bard and Faulkner 2001):

$$\Delta G = - nFE \quad (2.3)$$

Where, n : the number of moles of electrons transferred per mole of product generated. F : Faraday's constant or the charge of one mole of electron which is 96485 Col/mol. E : the potential energy required for product formation.

The formation of diverse hydrocarbon species directly from CO₂ and H₂O seems unfeasible and even stable at increasing temperatures (if not more unfeasible) in contrast with the case of H₂ and CO formation as the splitting potential of both CO₂ and H₂O decreases with temperature (Figures 2.2,2.4). This can be imputed to entropy change (ΔS) increasing (and ΔG decreasing by $\Delta G = \Delta H - T\Delta S$) at increasing temperatures for several reactions (2.1, 2.2). These involve the conversion of stable molecules (CO₂, H₂O) with low entropy to more random trend molecules of H₂ and CO (higher entropy) whereas this action is almost inverse in the case of hydrocarbon formation. It can be seen also from Figure 2.4 that CH₄ formation is slightly more feasible than longer chain hydrocarbons. The formation of CH₃OH from the gaseous CO₂ and H₂O reactants is even more difficult than the formation of other long-chain species at high temperatures (>300 °C).

In spite of that, the conversion of CO₂ and H₂O by co-electrolysis in molten salts (such as carbonate or hydroxide) can be more feasible and possibly affected by temperature as will be illustrated in detail later in this chapter.

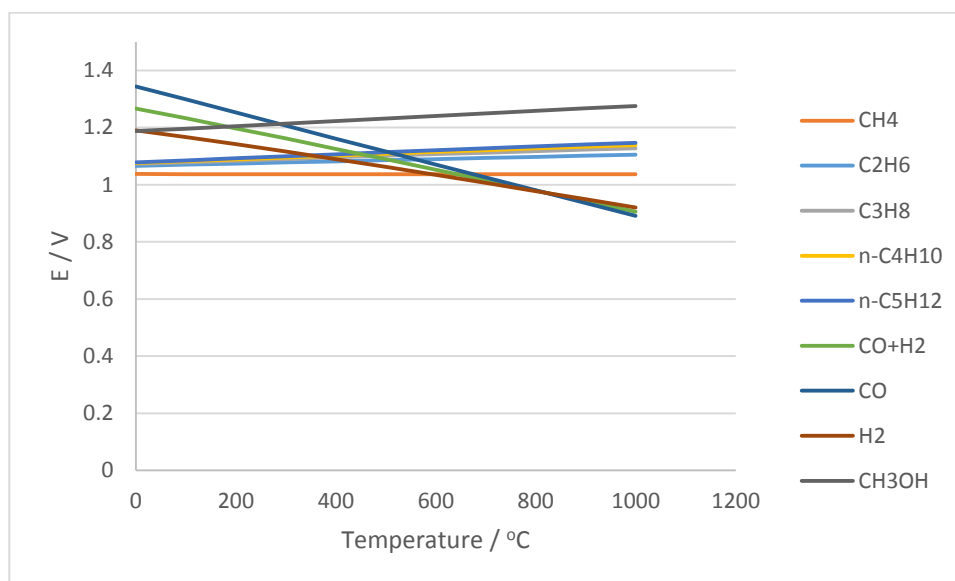


Figure 2.4. The thermodynamic potentials of fuel formation by electrolysis from gas phase reactants. The formation reaction is $x\text{CO}_2(g) + y\text{H}_2\text{O}(g) = \text{C}_x\text{H}_y(g) + (2x+y)/2 \text{O}_2(g)$ or $\text{CO}_2(g) + 2\text{H}_2\text{O}(g) = \text{CH}_3\text{OH}(g) + 2\text{O}_2(g)$ for hydrocarbon legends; $\text{H}_2\text{O}(g) = \text{H}_2(g) + 1/2\text{O}_2(g)$ for H_2 ; $\text{CO}_2(g) = \text{CO}(g) + 1/2\text{O}_2(g)$ for CO and $\text{CO}_2(g) + \text{H}_2\text{O}(g) = \text{CO}(g) + \text{H}_2(g) + \text{O}_2(g)$ for $\text{CO} + \text{H}_2$ (HSC Chemistry software (version 6.12; Outokumpu Research))

2.1. Background on the various process techniques for CO₂ recycling into fuels

As stated before in the last section, a considerable amount of energy (almost from electricity) should be consumed for the production of fuels from CO₂ and H₂O ultimately. Table 2.1 demonstrates the most efficient methods to convert CO₂ and H₂O into fuel with their pros and cons. The classification is based on their operating temperatures in ascending sequence and explanations about their energy consumptions and efficiencies. It is worth mentioning that, in this table, energy consumption is accounted per kg of H₂ production as a normal

Table 2.1: The economic specifications of modern techniques used for CO₂ and H₂O dissociation.

* To be explored in the future

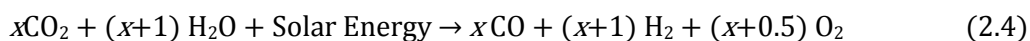
** The efficiency here is based on efficient use of heat to product formation.

Technique	Temperature	Energy consumption	Efficiency	Products	Advantages	Disadvantages	References
Aqueous electrolysis	70-100 °C	55 -138.2 kWh per kg of H ₂ produced.	Voltage efficiency 60-80%	H ₂ , CO, CH ₄ , C ₂ H ₄ , C ₂ H ₆ , CH ₃ OH, HCOOH	Relative low costs Non noble catalyst.	Lower durability Higher overpotential Low solubility of CO ₂ Formation of various by-products.	(Wang, Roberts et al. 2012; Carmo, Fritz et al. 2013)
Proton exchange membrane (PEM)	70-100 °C	13.4-80.7 Kwh/kg of H ₂ produced.	Voltage efficiency 60-74%	H ₂ , CH ₄ , C ₂ H ₄ , C ₂ H ₆	Longer term durability than aqueous electrolysis. Dynamic operation	Contain expensive metals Acidic corrosive environment. (Carmo, Fritz et al. 2013)	(Barbir 2005; Carmo, Fritz et al. 2013)
Electrolysis via molten salts	200- 1000 °C	N/A*	N/A	H ₂ , CO, C, CH ₄	Good heat transfer ability. Low capital costs	Slightly corrosive	(Lovering 1982)
Solid oxide electrolysis	800-1000 °C	50-60 kWh/kg of H ₂ produced.	70%	H ₂ , CO	High voltage efficiency. Non noble catalysts	Higher production costs Degradation of metal oxide and low durability	(Graves, Ebbesen et al. 2011; Redissi and Bouallou 2013)
Thermochemical cycles	700-2000 °C	Thermal heat from solar or nuclear reactor plus 23.5 kWh per kg of H ₂ produced.	16-25% solar to chemical conversion depending on the process. **	H ₂ , CO	High long term durability	Undesired side reactions. Energy losses through multiple steps Expensive materials due to the high temperatures	(Graf, Monnerie et al. 2008; Graves, Ebbesen et al. 2011)

unit for energy balance evaluation used in the most publicised investigations (Graf, Monnerie et al. 2008). A value of 120.5 MJ of heat is released for each kg of H₂ burned during combustion or any power generating process. This value is called the heating value of H₂. However, if some hydrocarbons are successfully produced from dissociation, the energy consumption will be lower because the heating value of hydrocarbons (for the volumetric basis at least) is bigger than that for H₂.

2.1.1. Thermochemical cycle

Thermochemical cycles are processes to dissociate and split H₂O and CO₂ through a series of thermally driven or solar-powered chemical reactions. Conventionally, a huge amount of heat besides an additional energy (like electricity) are needed to reverse the combustion reaction into the following reaction:



Hydrocarbon fuels can be produced then via the Fischer-Tropsch technique which processes the synthesis gas that consists of CO and H₂ at lower temperatures (200-500 °C) as follows:



It is worth mentioning that alkanes (C_xH_{2x+2}) are one of the various hydrocarbon products resulting from reaction 2.5. Due to the prospect of regeneration of CO₂ and H₂O after processing reaction 2.4, quenching of reaction products must be performed. To avoid that, two-step thermochemical

reactions can be done in a process called the thermochemical cycle (Abanades and Villafan-Vidales 2011). In this process, a two-step reaction cycle is established. The reduction of a metal oxide to a metal or a lower-valence metal oxide while emitting O_2 will occur in the first step at higher temperatures (up to 2000 °C) powered by concentrated sunlight or nuclear energy. In the second step, the reduced metal or metal oxide can be oxidised returning to the former situation spontaneously while in turn reducing CO_2 to CO or H_2O to H_2 in the lower temperature range (300-600 °C) as shown in Figure 2.5 (Chueh and Haile 2009; Graves, Ebbesen et al. 2011).

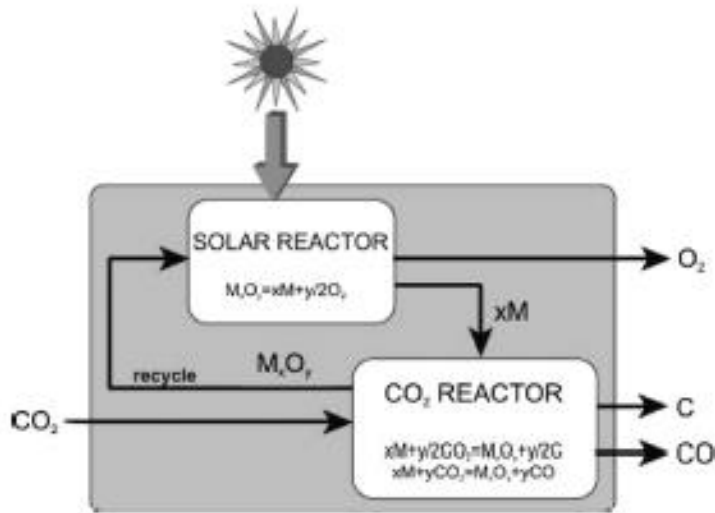
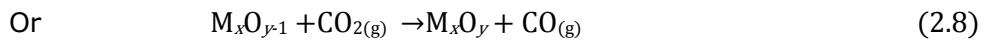
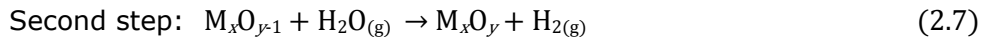
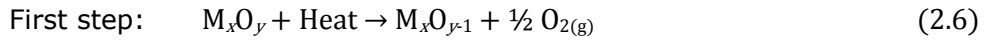
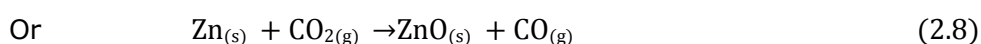
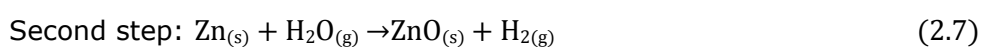
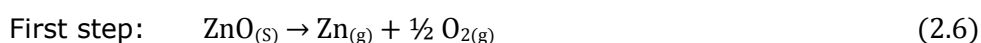


Figure 2.5. Schematic view of the solar powered thermochemical cycle to reduce CO_2 to CO or C via M_xO_y/M reactions. (Gálvez, Loutzenhiser et al. 2008).

Most metal oxides used in this case are ZnO, SnO and FeO. For ZnO, the zinc metal will be formed first in the gaseous state from the reduction of ZnO at temperatures of 1600-2000 °C in reaction 2.6. Subsequently, it must be quenched prior to the next step of water splitting (reaction 2.7) to H₂ gas at a temperature range of (300-400 °C) as shown for the ZnO/Zn cycle below (Ao, Wang et al. 2008):



The disadvantage of this cycle is the formation of a passivating layer of ZnO on the metal in the second step, thereby reducing the rate of reaction 2.7 (Gálvez, Loutzenhiser et al. 2008). In total, the problems of product separation (H₂, H₂O, C, CO, CO₂) and energy losses through the multiple step process are encountered in all metal oxide cycles used in this technique, thus reducing the general energy efficiency.

2.1.2. Electrolysis.

In electrolysis, an electrical current is passed through a cell to produce the requisite electrical energy to facilitate the reaction. An electrolytic cell uses electricity to dissociate CO₂ and H₂O. Generally, this dissociation will be performed in one step like a semi-batch reaction. Another attractive aspect of this technique is the ability to separate the dissociation products easily into two electrode compartments. One compartment is engaged by the negative

electrode (cathode) to adsorb the cathodic gases on it before the production whereas the other compartment is for the positive electrode (anode).

It is worthwhile to mention that the electrode reaction can be more likely interrupted than a normal reaction in the solution or in the gaseous phase. The latter is called a homogeneous reaction because it takes place everywhere in the solution at the same rate. Alternately, the electrode reaction is heterogeneous in nature, occurring only at the electrode/electrolyte interface with a rate affected by the mass transfer to the electrode itself in addition to the usual kinetic variables (Bard and Faulkner 2001). Therefore, the normal reaction is relatively faster than the electrochemical reaction. Electrolysis can be carried out at either low or high temperatures, depending on the electrolyte used and the product desired.

2.1.2.1 Low temperature electrolysis.

Generally, the chemical reactivity of CO₂ is low. However, the equilibrium potential of CO₂ reduction to hydrocarbon species or CO is not very negative as compared to that of the hydrogen evolution reaction (HER) in an aqueous solution as will be illustrated later. The electrolysis at lower operating temperatures (up to 100 °C) is characterised with a significant feature as it does not involve a great amount of heat (Noda, Ikeda et al. 1990). Actually, CO₂ conversion is highly limited by reaction kinetics rather than thermodynamics. Many types of electrolysis at low temperatures have addressed the transformation of CO₂ into CO or hydrocarbons and can be classified as follows:

Aqueous solution electrolysis

Some investigations on CO₂ reduction have been done by bubbling the gas inside an aqueous carbonate or bicarbonate electrolyte. Copper or some noble metals like platinum should be used in this application as a cathode material to catalyse the reduction. Small amounts of HCOOH, CO, CH₄, CH₃OH and C₂H₄ products were discovered from the electro-catalytic reduction of CO₂ and H₂O (Hori, Murata et al. 1989).

During electrolysis in an aqueous solution, several reactions can occur on the cathode including the reduction of CO₂ and H₂O together into fuel products at a pH value of 7 and 25 °C (Ganesh 2014) as follows: (potential vs. the Normal hydrogen electrode (NHE))

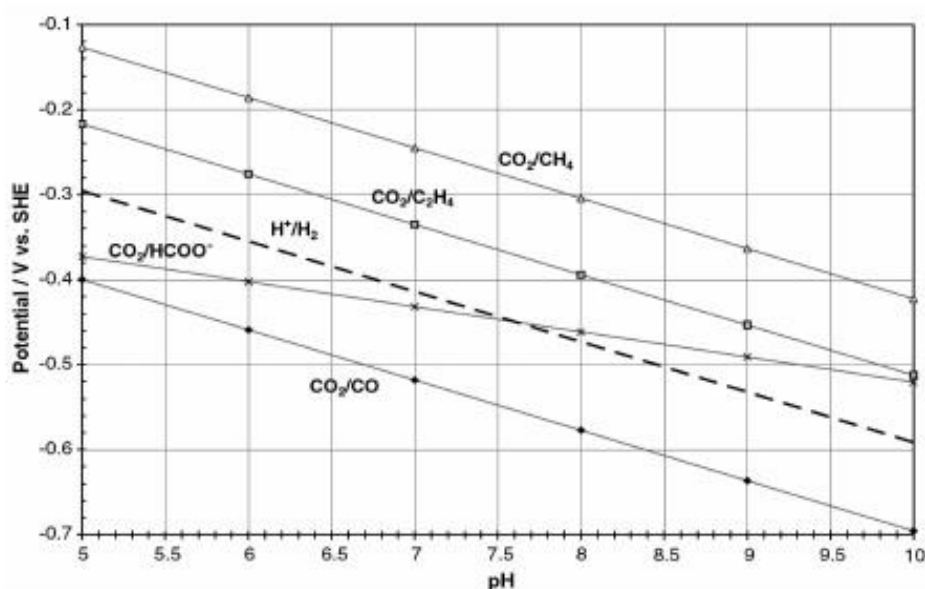
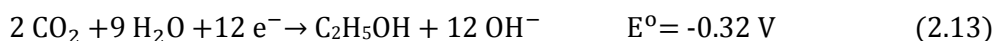


Figure 2.6. The equilibrium potentials vs. pH for the overall reduction reactions of CO₂ at 25 °C. (Gattrell, Gupta et al. 2006)



The variation in potential of the above reactions with differing pH values can be shown in Figure 2.6. Actually, the final reaction (2.14) of the hydrogen evolution reaction (HER) is kinetically faster and more likely to occur than the other reactions during hydrocarbon formation.

The potential applied (or energy required) to commence reduction should be higher than the theoretical equilibrium potential (E^0). Therefore, an overpotential (η) above E^0 is necessary to overcome the activation energy barrier and bubble formation due to gas product generation on the cathode. It is very important for any electro-reaction to utilise the entire amount of available electrical energy to obtain the maximum yield of the product.

Methanol (CH_3OH) was one of the reduction products and can be formed as follows:



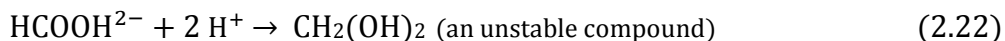
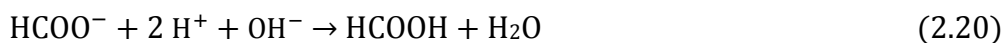
In the example of methanol above, it can be seen that one hydrogen ion (H^+) is needed to be transferred to the cathode for each electron required for the formation of the fuel molecule. The last reaction is more preferable at $\text{pH} < 7$ or acidic solutions (Hori, Murata et al. 1989).

The theoretical (equilibrium) potential (E^0) decreases (being more positive) with increasing pH according to the Nernst equation:

$$E = E^0 - \frac{RT}{6F} \ln \frac{[\text{CH}_3\text{OH}]}{[\text{H}^+]^6 P_{\text{CO}_2}} \quad (2.16)$$

Kinetically, the transfer of 6 electrons to perform reaction 2.15 is difficult as it requires a very selective catalytic system to promote methanol formation. First of all, as the equilibrium potential of CO_2 reduction into methanol (reaction 2.16) is very close to the potential of HER, the supplied potential will be shared by HER (reaction 2.14) as stated before on the cathode, in addition to CO_2 reduction as well. Basically, hydrogen formation can be considered to be a major side reaction reducing the hydrocarbon yield.

Moreover, it has been found that a sequence of intermediate reactions for CO_2 reduction to methanol is more probable in order to obtain the net reaction of methanol formation (reaction 2.16) (Ganesh 2014):



CO₂ reduction through the last sequence does not take place easily as the first intermediate species (CO_2^-) is formed at a relatively high negative potential (-1.6 vs. NHE) increasing the actual (practical) potential for the whole methanol formation process (Cook, MacDuff et al. 1988). Nevertheless, a selective catalyst should be used at least to suppress hydrogen formation and promote the last sequence (reactions 2.17-24) effectively for which the first step, in particular (reaction 2.17), is considered to be the rate-determining step of the whole process (Wenzhen 2010).

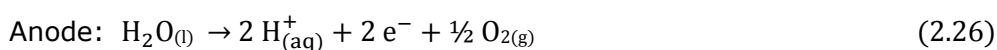
In general, the selectivity of the hydrocarbon species in the product changes depending on the metal used (as a catalyst) for cathode materials such as Ag, Cu or Au (Graves, Ebbesen et al. 2011).

Besides the low solubility of CO₂ gas in this medium and the high overvoltage values that were used to perform these reactions (> 1.0 V vs. the NHE) due to their slow kinetics, the high initial selectivity of products and reactivity of the metal electrode will be lost after a short time of electrolysis. This is because of surface contamination with unseparated products (from the cathode) or carbon particles dissociated from the adsorbed CO product leading to low productivity and selectivity towards hydrocarbons (Hori, Konishi et al. 2005).

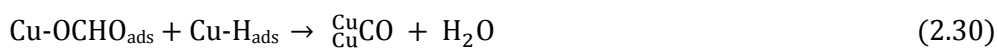
Proton exchange membrane

To mitigate the poisoning of the metal electrode and the progressive production of H₂ over CO₂ reduction products, a special technique called solid polymer electrolyte (SPE) for CO₂ reduction was developed (Nishimura, Yoshida et al. 1995). It can be seen from reaction 2.15 that hydrogen ions or protons (H⁺) are the only ions required to be transferred from the anode for hydrocarbon or H₂ formation. The anode and cathode compartments are separated from each other by a SPE membrane working as a medium for the transfer of H⁺ ions with

no additional species being formed on the anode. The electrolyte used is a CO₂ saturated aqueous solution of biocarbonate salt such as KHCO₃ (to prevent the likely CO₂ permeation across the SPE). The cathode is obtained by copper deposition at one surface of the SPE membrane while the other surface is exposed to the anolyte (the part of electrolyte on the anode side) solution as shown in Figure 2.8. Another function of the membrane is to prevent product oxidation from the opposite action. Actually in this technique, protons are mostly reduced to H₂ gas at the cathode while O₂ is released from the anode according to the following reactions:



When applying CO₂ gas on the cathode surface, the initial or rate-determining step is the direct reaction of electrochemically generated chemisorbed hydrogen with the adsorbed CO₂ (reaction 2.29). Subsequently, a lesser amount of cathodic overpotential would be utilised to promote CO₂ reduction compared with the previous aqueous solution case (Cook, MacDuff et al. 1988).



CO can be deliberated from the cathode surface (reaction 2.31) or transferred to CH₄, C₂H₄ or C₂H₆ through the scheme shown in Figure 2.7 (Cook, MacDuff et al. 1988).

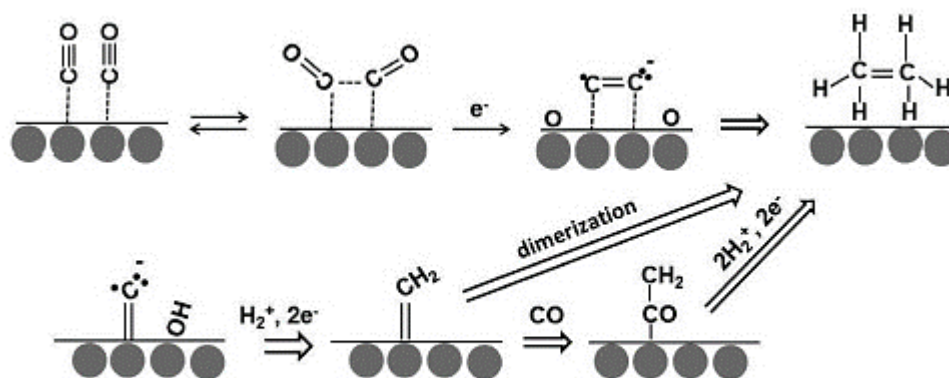


Figure 2.7. The proposed reaction mechanism for producing C_2H_4 and C_2H_6 . The grey particle is a Cu atom (Li 2010).

The main products from this technique are C_2H_4 and C_2H_6 with faradaic efficiencies less than 2 and 0.17% respectively, at all cell voltages applied (Cook, MacDuff et al. 1988). Nevertheless, $HCOOH$ and CO products were obtained as well.

The main concern with regards to the SPE technique though is that it uses expensive materials such for the membrane and noble metals like platinum as the cathode catalyst instead of copper to obtain practically viable current efficiency.

A recommended design for the SPE cell is shown in Figure 2.8.

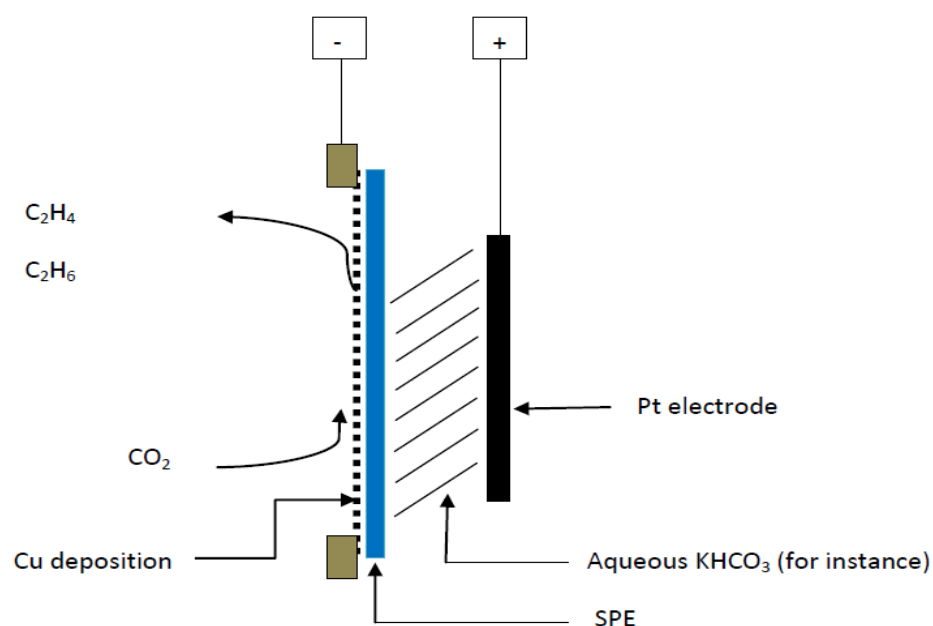


Figure 2.8. Schematic shape of SPE (Cook, MacDuff et al. 1988)

2.1.2.2. High temperature electrolysis.

Generally, performing the electrolysis (of H_2O or CO_2) at higher temperatures ($>200\text{ }^{\circ}C$) will enhance not only the thermodynamic factors of the process but also the reaction kinetics. With increasing temperature, a high portion of heat and thus a smaller portion of electricity is needed to perform dissociation.

Also, high temperature electrolysis will reduce the need for more expensive catalytic material due to faster reaction kinetics leading to lower capital costs (Graves, Ebbesen et al. 2011). However, some catalytic metals can still be used as a cathode or anode material depending on the electrolytic conditions required to enhance the performance of the cell towards CO_2 reduction (for instance) (Kaplan, Wachtel et al. 2010) .

Two types of cells can be used for high temperature electrolysis: molten salt electrolysis cells and solid oxide electrolysis cells (SOEC).

Molten salt/eutectic mixtures

Molten salts are used widely in various industry applications. Due to their unique properties of thermal stability and relatively low vapour pressures (Janz 1967), these salts provide a wide range of uses in high temperature chemistry, particularly in the case of faster reaction rates.

Furthermore, in connection with the ability to dissolve different kinds of inorganic species such as oxides, nitrides, carbides and other salts; they have been used in electrometallurgy, metal coating, the treatment of waste and energy conversion.

In contrast with aqueous solutions, the apparently wider potential window between the decomposition limits in molten salt media results in the formation of highly electronegative elements or the scuttling of highly electropositive components.

Nowadays, laboratory research in energy storage is deeply focused on fused salts. Materials such as Carbon Nanotubes (CNT), lithium and sodium batteries and lithium hydrogen energy cycles can be produced successfully in molten salts exhibiting high capacity energy storage.

The modern investigations in molten salts has led to the foundation of the large-scale electrochemical extraction of aluminium and other metals in the last century. In nuclear applications (for instance), molten salts have been used in uranium extraction and more active actinide separation processes in addition to the treatment of radioactive waste (Stevenson, Hu et al. 2014).

Molten salts in the form of high-capacity heat storage substances, can be used (as stated before) for metal treatment processing. This treatment can be performed in two ways: bulk metal modification (e.g. redistribution of elements and annealing) and metal surface modification.

Eutectic mixtures of molten salt compositions are mixtures of two or three different salts that aim to obtain the minimum melting point. In the electrochemical reduction of CO_2 (for instance) via molten salt technology, different types and compositions of molten salt mixtures can be used to achieve this aim. These salts may include primary, eutectic binary and ternary molten carbonate mixtures.

From Figure 2.9, it can be seen that the minimum melting temperature for the Li_2CO_3 - K_2CO_3 binary salt is 488 °C at a ratio of 62:38 mole% whereas, for the ternary salt of Li_2CO_3 - Na_2CO_3 - K_2CO_3 , the minimum melting point is 397 °C at the ratio of 43.5:31.5:25.0 mol% (Janz and Lorenz 1961). These salts are called eutectic because the composition of the binary or ternary salts are chosen to have the lowest possible melting point.

There is lack of relevant literature on the reduction of CO_2 to hydrocarbons in molten salts, particularly in the case of the co-reduction of CO_2 with H_2O . However, many investigations have recorded the reduction of CO_2 to deposited carbon or CO to mitigate higher CO_2 emissions. An example of this is the carbon deposition reported in molten Li_2CO_3 - Na_2CO_3 for example by Bartlett and Johnson (1967).

Moreover, molten salts have been employed as an electrolyte for H_2O reduction to H_2 gas in parallel with an aqueous solution.

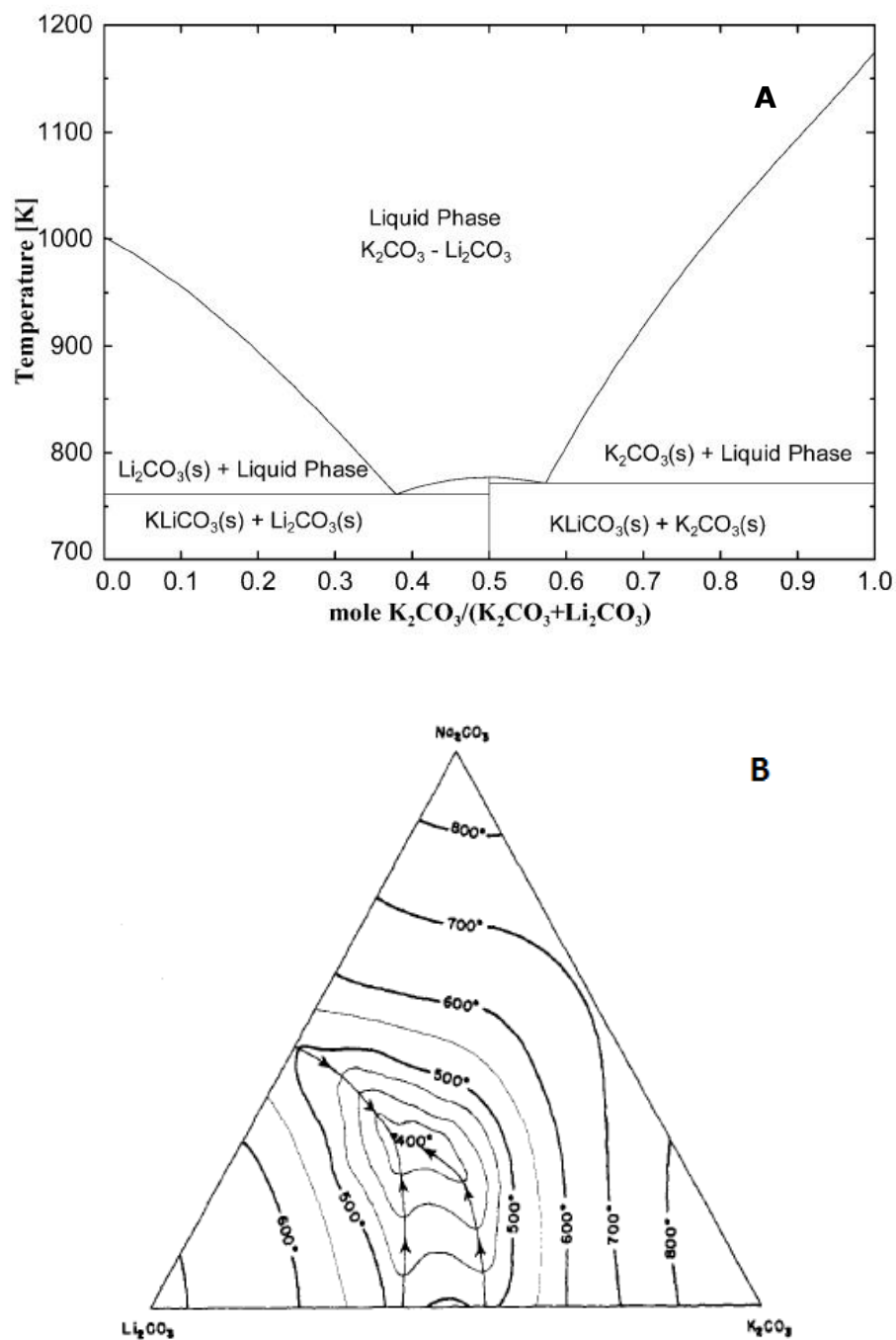


Figure 2.9. Phase diagram of (A): $Li_2CO_3 - K_2CO_3$ binary molten salt (Ochoa-Fernández, Rønning et al. 2008) (B): $Li_2CO_3 - Na_2CO_3 - K_2CO_3$ ternary molten salt. (Janz and Lorenz 1961)

Comparing the performance to an aqueous solution, it was found that the catalytic combination of two adsorbed hydrogen atoms (reaction 2.33) at the metal cathode (gold or platinum) in molten KHSO_4 is the most operative step (likely to proceed rather than the one-transfer electron reaction step) in the cathodic evolution of hydrogen (Shams El Din 1962).

Therefore, after the one-transfer reaction of atomic hydrogen formation suggested in both mediums:



The combination reaction that is preferred in molten salt is as follows:



With lower over-potential represented by the Tafel equation as follows:

$$\eta = a - 2.303 RT/2F \log i \quad (2.34)$$

where; η : overpotential (V), a : constant, which is equal to $2.303 RT/2F \log i_0$.

i_0 : the exchange current, which is a current of the reversible water dissociation reaction and can be expressed by the following equation:

$$i_0 = FA k^0 e^{-\alpha f(E_{\text{eq}} - E^0)} \quad (2.35)$$

Where; F : faraday's constant, A : surface area of the electrode at which the reaction takes place, k^0 : the standard rate constant, α : the transfer coefficient and its value lies between 0 and 1 for the one-electron transfer reaction. Therefore, the exchange current (i_0) is a function of the nature of the electrode material. The Tafel slopes obtained from KHSO_4 experiments were plotted in Figure 2.10.

Meanwhile, the last step of the process (reaction 2.33) indicates that the most likely rate determining step for H_2 formation in an aqueous solution of the same salt ($KHSO_4$), occurs with relatively higher overpotential and activation energy than that observed for the molten salt (Delahay and Tobias 1966). Also, the exchange current (i_0) of hydrogen evolution in the molten salt is significantly lower than the corresponding values in aqueous media.

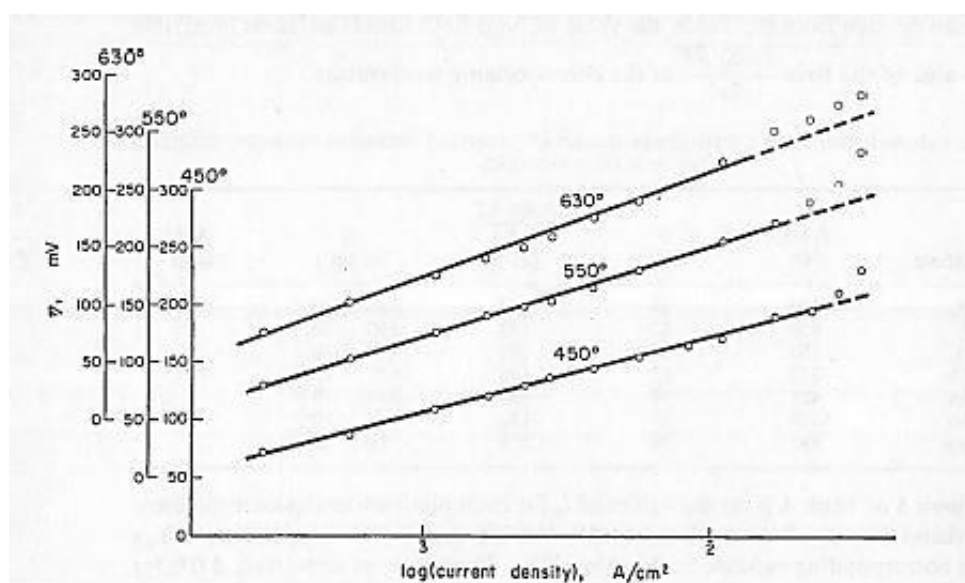


Figure 2.10. Overpotential plotted for the evolution of hydrogen on platinum in molten $KHSO_4$ as a function of $\log$ (current density) and temperature. (Shams El Din 1962)

The key advantages of using molten salts for the co-reduction of CO_2 and H_2O are the lower melting point of the eutectic mixture as hydrocarbon formation is preferred at low temperatures and the enhanced ability and capacity of the salt to absorb CO_2 gas, particularly in molten carbonates. Thus, there are

different compositions of different molten salt types that can be used to achieve this aim. In a molten salt medium, corrosion (in general) and safety are the serious problems for material compatibility at elevated temperatures (Lovering 1982). Eutectic ternary mixtures of molten carbonates have received most attention for use in CO₂ reduction experiments due to their lower melting point compared to single and binary mixtures (Janz and Lorenz 1961).

Molten salts in general have unique characteristics in terms of catalysing the various transformation processes besides their electrolytic features. Regarding the conventional conversions:

1. Molten carbonates such as Li₂CO₃, Na₂CO₃ or K₂CO₃ can serve as a catalyst in the methane sole reforming (cracking) process to H₂ and CO at 900 °C. The ternary mixture of molten Li₂CO₃, Na₂CO₃ and K₂CO₃ in the ratio of (43.5:31.5:25.0) in mole% is preferred in this case to increase the CO production rate and decrease CO₂ that is released with the products (Ao, Wang et al. 2008).

2. This ternary mixture of molten carbonates has also been employed in the dry reformation of CH₄ with CO₂ using FeO as a catalyst at 950 °C and in two stages, according to the following reactions:



for a high feed flowrate, and



for a low gas feed flowrate (Gokon, Oku et al. 2002).

3. Molten salts can be used to catalyse the partial oxidation of CH₄ to C₂ hydrocarbons (C₂H₄ and C₂H₆). A mixture of CH₄ and O₂ at a ratio of CH₄:O₂=3:1 was bubbled through the molten hydroxide Ba(OH)₂ (Moneuse, Cassir et al. 1990) or binary molten mixture of Na₂CO₃-K₂CO₃ (Moneuse, Cassir et al. 1992) at 800 °C. The selectivity for C₂-products was higher in the case of molten carbonate whereas the yield itself was higher in the Ba(OH)₂ case. The formation of higher carbon fuel molecules such as C₃ and C₄ can be obtained at lower temperatures using mixed KCl-LiCl molten salts at 550 °C (Branco, Lopes et al. 2012). Therefore the lower the temperature, the higher the selectivity for unsaturated products (such as C₂H₄, C₃H₆) (Branco, Lopes et al. 2012). If free oxygen gas which is involved in the feed gas is not preferred, partial oxidation of CH₄ can be done through the zinc extraction route from ZnO according to reaction 2.38:



Reaction 2.40 is endothermic and was conducted at 930 °C via several intermediate reactions producing C, CO₂ and H₂O. The binary Na₂CO₃-K₂CO₃ molten mixture was used as a catalyst to perform the above gas (CH₄)-solid (ZnO) reaction.

4. The above processes can be conducted in a solar reactor in which the molten salt can work as a medium to receive and transfer the solar heat required for conversion. It can avoid the loss of heat outside the reactor due to the large heat capacity of the salt reserved. Also, the heat fluxes will be distributed

through the molten salt without any hot spots or heat waves as found in conventional fixed or fluidised bed reactors (Gokon, Oku et al. 2002).

5. Carbonate containing salts are used as a solution and as ingredients for the preparation of some powdered catalysts. K_2CO_3 for instance is used to produce an Fe-activated catalyst with 25% K for the Fischer-Tropsch synthesis illustrated above (Hans Schulz 1998). The alkali metal in the catalyst composition can play a significant role in changing the shape or nature of the hydrocarbon produced from paraffinic to oxygenated organic materials during the Fischer-Tropsch process at 250 °C.

Molten salts have been used also as an electrolyte in fuel cells due to their long life time and high durability (Koh, Seo et al. 2002).

In conclusion for the electrochemical characteristics, molten salts are preferred for the reduction of carbon dioxide and water compared with aqueous electrolytes due to:

1. The high solubility of CO_2 gas inside the melt.
2. The ability of using continuous process electrolysis as well as the separation of cathode and anode gases (Kaplan, Wachtel et al. 2010).
3. The high current efficiency.
4. Lower overvoltage.
5. Wide potential window.

Solid oxide electrolysis

High temperature (850-950 °C) electrolysis of CO_2 or/and H_2O in a solid oxide electrolysis cell (SOEC) is carried out to produce the syngas which is a gaseous mixture of H_2 and CO. Hydrocarbons can be obtained afterwards from the

syngas via the Fischer-Tropsch synthesis (reaction 2.5) (Becker, Braun et al. 2012). Due to the high temperature conditions, CO or H₂ may be produced also from the water gas shift reaction (WGS) or the reverse of the WGS reaction (RWGS) as follows:



It is worth noting that reaction (2.42) can be feasible at temperatures around 817 °C as the Gibbs free energy of reaction (ΔG_r) starts to be negative above this point. The cathode and anode reactions of the solid oxide electrolysis cell (SOEC) are summarized below.



Or



The most common material composition of typical SOECs uses a porous metal ceramic of the Ni-YSZ (yttria-stabilised zirconia) composite as a cathode and the lanthanum strontium manganite with YSZ as an anode, sandwiching a dense ceramic electrolyte of YSZ between the two layers of the cathode and anode. YSZ was used as an electrolyte to conduct O²⁻ ions at high temperature (Zhan, Kobsiriphat et al. 2009) as shown in Figure 2.11.

It has been found that the Ni-YSZ cathode can only operate under reducing conditions (such as the flow of H₂ or CO over it) to avoid oxidation to NiO, thereby causing a loss of electronic conductivity (Redissi and Bouallou 2013).

The introduction of H₂ (or CO) gases will definitely reduce the entire process efficiency. However, some investigations used other types of cathode material such as (La_{0.75}Sr_{0.25})_{0.95}Mn_{0.5}Cr_{0.5}O₃ (LSCM) as an active material to avoid the addition of a reducing agent, but they were unsustainable in the long term at a strongly reducing condition that occurs at the cathode (Kim, Corre et al. 2008).

The composition of the outlet gas product depends on three parameters: electrolysis temperature, applied voltage and feed gas composition. At higher applied voltages (>1.5 V), coke formation (carbon deposition) can occur on the cathode as follows (Sun, Chen et al. 2012):

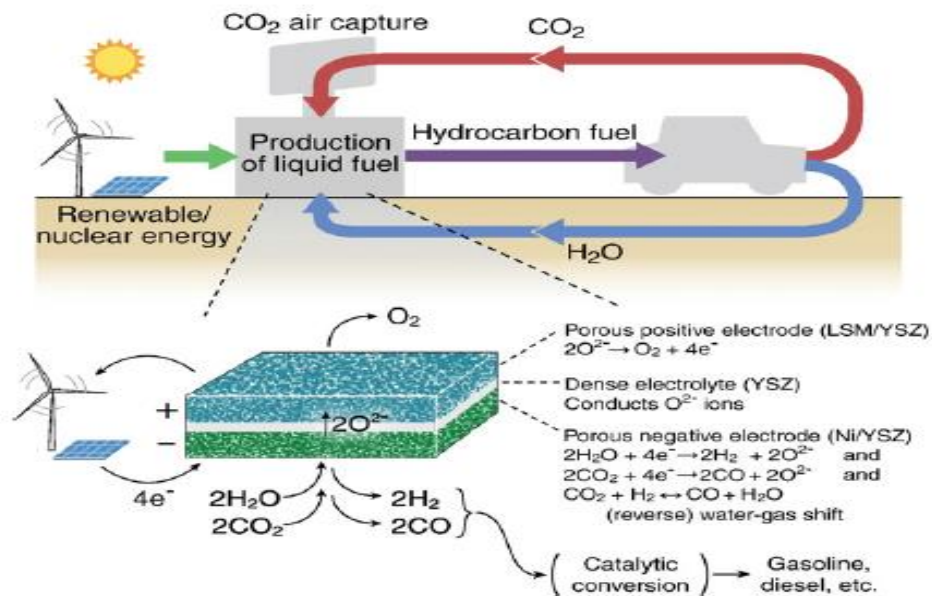


Figure 2.11. Design of co-electrolysis of CO₂ and H₂O in SOEC considered as a part of renewable fuel cycle. The electrode reactions are also provided. (Graves, Ebbesen et al. 2011)

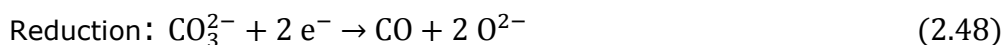
Regarding the electrolytic temperature employed, CH₄ can be formed at temperatures lower than 700 °C though the rates of CO₂ and H₂O reduction are relatively slow at this temperature (Redissi and Bouallou 2013):

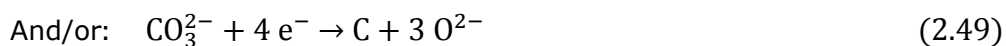


In the co-electrolysis of CO₂ and H₂O, the resistance for CO₂ electrolysis is higher than that for H₂O electrolysis, leading to the formation of CO from the RWGS reaction due to the high content of H₂ (Graves, Ebbesen et al. 2011). The instability of the Ni-based electrode against the oxidising conditions in SOEC is a major issue that needs to be resolved before any large scale commercial use of these cells. Furthermore, the performance degradation of the electrode structures due to sintering and agglomeration at high temperature operations results in greater disadvantages of SOEC usage as a promising technique for effective reduction of CO₂ (Graves, Ebbesen et al. 2011).

2.2. Reaction mechanisms of electroreduction of carbon dioxide and water to hydrocarbons in molten salts.

During the early investigations of valuable products from CO₂ electrolysis in molten salts, H₂ gas was found accompanying the products of electrolysis in the ternary molten carbonate mixture of Li, Na and K₂CO₃ for instance, at temperatures upwards of 560 °C (Lorenz and Janz 1970). The existence of H₂ is noted due to the contaminated nature of moisture in the salt. This was not dried prior to electrolysis and the corresponding reactions are as follows:





The oxidation reactions will be the same reaction 2.45 and/or



Then in the presence of moisture, reaction 2.41 can take place,

or



Therefore, after the electrochemical reduction of CO_2 (or carbonate ion) to CO or carbon on the cathode in the molten salt (reactions 2.48, 2.49), H_2 can be formed possibly by the reaction of CO with H_2O (WGS (2.41)) or with hydroxide ions (reaction 2.52) found in molten salt due to reaction (2.51). O_2 gas will be produced at the anode by reaction (2.50 or 2.45). It is worthwhile to mention that CH_4 will be generated if the temperature is lower than 550°C based on Gibbs free energy for the following reaction:



Or via the Fischer-Tropsh process mentioned earlier (reaction 2.5), CH_4 can be produced consequently as follows:



On the other hand, H_2 gas can be formed from the dimerization reaction of two hydrogen atoms adsorbed at the cathode from the reduction of H_2O (Kanzaki and Takahashi 1975) or HCO_3^- (formed by reaction 2.55 in molten carbonate)

(White and Twardoch 1984) through the one electron transfer reaction as follows:



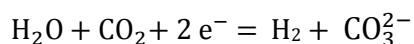
or



Then the combination (dimerization) reaction (2.33) can occur.



Therefore the overall reaction can be concluded as:



In one recent investigation, long-chain hydrocarbon species (such as C_2H_4 , C_3H_6 and C_4H_8) were found in the cathodic product beside H_2 , CO and CH_4 during electrolysis conducted in a $\text{Li}_{0.85}\text{Na}_{0.61}\text{K}_{0.54}\text{CO}_3/0.08\text{LiOH}$ molten salt mixture at 450°C and 2.5 V (Wu, Liu et al. 2017) (Figure 2.12). Basically, the salt mixture in question is determined as 0.08 mole of LiOH for each mole of the ternary carbonates ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$) with composition 43.5:31.5:25.0 mol%.

However, the distinction of hydrocarbon species in terms of the type (saturated or unsaturated) and molecular weight, has not been addressed closely. Various experiments were conducted in this investigation employing different compositions of the alkali metal (Na, K, Li) carbonates and hydroxides at different applied voltages (2-3.5 V) at 450°C .

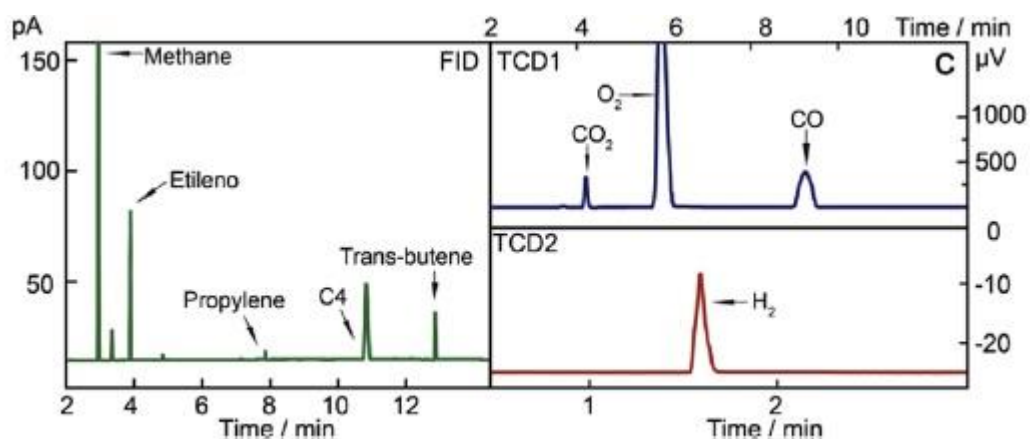


Figure 2.12. The chromatographic signals of FID, TCD1 and TCD2 for the gas product obtained from the electrolysis of $\text{Li}_{0.85}\text{Na}_{0.61}\text{K}_{0.54}\text{CO}_3/0.08\text{LiOH}$ molten salt mixture at 450 °C and 2.5 V (Wu, Liu et al. 2017)

It was claimed that CO_2 and H_2O can be introduced to compensate for the concentration of carbonate and hydroxide salts consumed during electrolysis. In general, it can be confirmed that decreasing the ratio of hydroxide to carbonate in the molten salt mixture leads to an increase in CH_4 (or hydrocarbon product) content and a decrease in the H_2 level in the cathodic gas output (Wu, Ji et al. 2016). The concentration of CH_4 gas can increase with temperature up to 600 °C.

After the confirmation of CH_4 and hydrogen gas formation, two further mechanisms were suggested to justify the prospective generation of hydrocarbon species in molten salts:

1. Through methane partial oxidation

Many authors have studied the regeneration of carbonate ions inside the molten salt (particularly molten carbonate) when oxide ions are available to react with carbon dioxide gas as follows (Ingram, Baron et al. 1966), (Lorenz and Janz 1970):



The carbonate ions here can act as a solvent in the acid-base solution. The molten salt will be described as more acidic if it is covered by the feed CO_2 gas at high concentrations during electrolysis. In contrast, when the gas feed is CO_2 -lean, the salt will be described as more basic with a high O^{2-} content (Lorenz and Janz 1970). In some molten salt mixtures like chlorides, the anode metal should be covered by a solid oxide layer such as ZrO_2 to transfer oxide ions through the layer and avoid direct contact between O_2 gas produced on the anode and the surrounding molten salt (Otake, Kinoshita et al. 2013). In this case, at a non-layered anode rod, other active oxide ions like (O_2^{2-} or O_2^-) can be formed in the melt as follows:

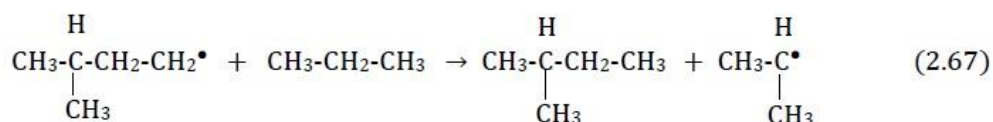
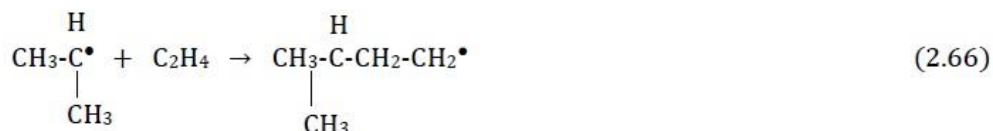
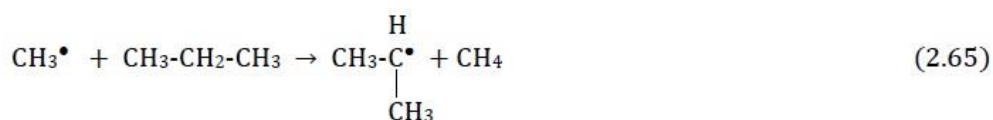


The last active oxide ion, O_2^{2-} , plays a significant role in catalysing the partial oxidation of CH_4 to C_2 hydrocarbon fuels for instance in the molten mixture of Li_2CO_3 - Na_2CO_3 molten salt at 700-850 °C, according to the following steps where a methyl radical ($\text{CH}_3^\bullet$) must be initially formed (Frangini and Masi 2016):





It is worthwhile mentioning here (apart from molten salt case) that the methyl radical or any other alkyl radical plays a major role in the formulation of large hydrocarbon species from paraffins during the thermal alkylation process, even in the absence of a catalyst at temperatures as high as 500 °C as follows (Groggins 1958):



It is recognised that the last radical $\text{CH}_3\text{CH}^\bullet\text{CH}_3$ in reaction 2.65 can attack other hydrocarbon molecules such as alkanes (C_3H_8) or olefins (C_2H_4), producing large hydrocarbon molecules such as (C_5H_{12}) in reaction 2.67 or alternately, even larger hydrocarbon molecules (Groggins 1958).

In the case of molten hydroxides, however, H₂ can be formed ultimately and directly on the cathode at moderate temperatures (220-400 °C) (Divisek, Mergel et al. 1980; Pier G. Zambonin 1981):



It can be noted in the above discussion that CH₄ is not formed directly from electrolysis at all. Furthermore, H₂ and CO gases can be reformed to hydrocarbons via other reaction techniques such as the water gas shift reaction (WGR) (reaction 2.41) or the Fischer-Tropsch reaction (reaction 2.5). For the WGS reaction which is endothermic in nature, CO can react with a sufficient amount of water vapour to produce H₂ gas, taking advantage of the unique thermal and chemical properties of molten salts. Moreover, metals such iron, nickel and titanium serving as an inert cathode in molten salts, may function as a catalyst to drive the Fischer-Tropsch reaction forward (reaction 2.5) (Wender 1996). However, the conversion of syngas (H₂ and CO) by the former process depends on the partial pressure of both H₂ and CO gas.

2 Through the reaction of H atoms with carbon.

It has also been confirmed that atomic hydrogen (H) obtained by thermal dissociation of H₂ gas can react with heated carbon at different temperatures to produce some hydrocarbon species in a reactor arranged as shown in Figure 2.13 (Snelson 1974). The main product was CH₄ with traces of C₂H₄, C₂H₆, C₃H₆ and C₃H₈. The thermal dissociation of H₂ was performed at 2300 °C in a tungsten effusion tube with 0.03 inches ID and inserted with three tungsten wires of 0.01 inches diameter to increase the resident time of the H₂ inside the tube. The maximum hydrocarbon yield was obtained at temperatures

around 500 °C. It was reported also that hydrocarbon formation was possibly from the attack of H to freshly adsorbed carbon species such as CO, CO₂ or some hydrocarbons rather than the reaction of H with the carbon target itself in the reactor. The low flowrate of H₂ feed was preferred here to avoid the recombination of two H atoms into H₂.

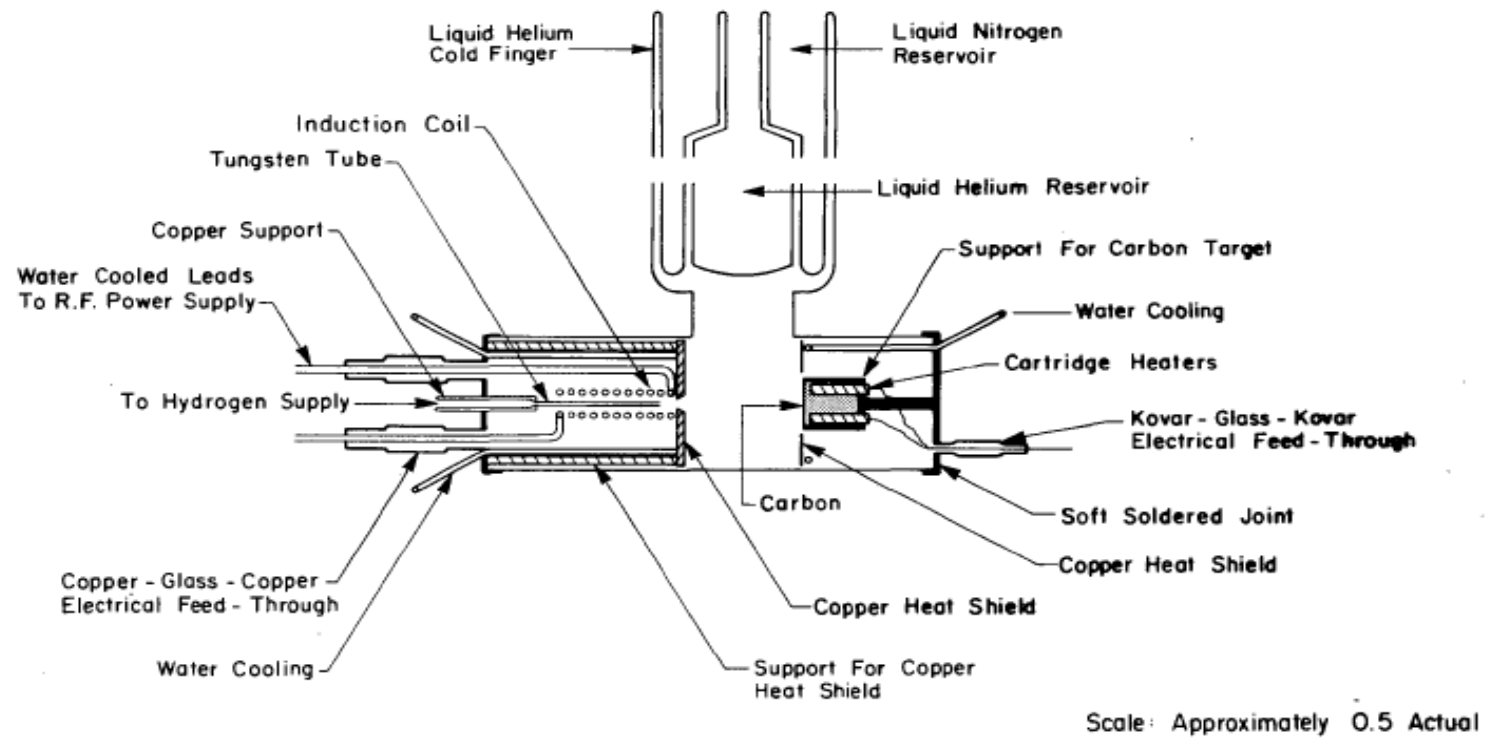


Figure 2.13. Schematic configuration of the atomic hydrogen-carbon reaction cell. (Snelson 1974)

2.3. Effects of electrolytic conditions on the reduction process in molten salts

2.3.1 Molten salt type and composition

The type of molten salt has an important effect on electrolysis and hydrocarbon formation afterwards. These fall into the following categories:

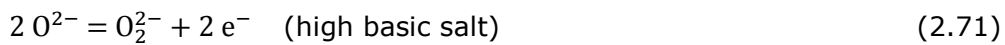
2.3.1.1. Molten carbonate salts.

Carbonate salts are widely used for carbon deposition. High specific surface areas of carbon nano-powders can be obtained from the electrolysis of carbon dioxide alone (without water) using the various eutectic mixtures of Li_2CO_3 , Na_2CO_3 and K_2CO_3 listed in Table 2.2 at the specified temperature range of 450-700 °C.

Table 2.2. Molten carbonate salts and their use for carbon deposition.

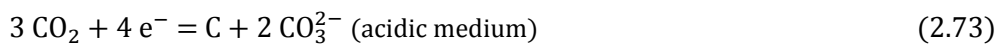
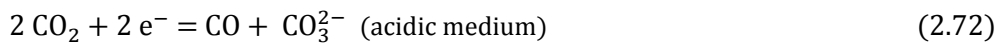
Author	Molten salt mixture	Temperature, °C
(Ingram, Baron et al. 1966)	$\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (43.5:31.5:25.0) mol%	600
Kaplan, Groult et al. (2001); Kaplan, Groult et al. (2002)	$\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (43.5:31.5:25.0) mol%	450
(Lantelme, Kaplan et al. 1999)	$\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (43.5:31.5:25.0) mol%	450
(Lorenz and Janz 1970)	$\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (43.5:31.5:25.0) mol%	500
(Chery, Albin et al. 2014)	$\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ (52:48) mol%	600
(Chery, Albin et al. 2014)	$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (62:38) mol%	575

For thermodynamic considerations, oxidation reactions will be performed in molten carbonates according to the acidity level or partial pressure of CO₂ gas (P_{CO_2}) over the salt itself (as illustrated in section 2.2). When the acidity decreases in the salt, the products on the anode can change from oxygen gas (O₂) to superoxide ions (O₂⁻) or peroxide ions (O₂²⁻) with a descending sequence as follows:



Therefore, oxygen gas is the stable form of oxidation in high acidic media (reaction 2.69).

Regarding the reduction reactions, it can be noticed that in the absence of H₂O, cathodic limits can result from the reduction of CO₃²⁻ (or CO₂ in acidic medium) to C and CO or from the reduction of the alkali cation into metal according to the following reactions:



Experimentally as shown in Table 2.2 above, Lorenz and Janz (1970) reported that a little amount of H₂ gas was found in the off-gas product as a result of the moisture in the salt as mentioned previously.

White and Twardoch (1984) on the other hand studied the effect of H₂O addition with CO₂ using the CO₂/O₂ reference electrode in two conditions,

higher carbon dioxide concentration (>75 vol%) and much lower concentration (<25 vol%). They found that, in the second condition, hydrogen atoms can be adsorbed on the gold electrode at $460\text{ }^{\circ}\text{C}$ using the ternary molten carbonate mixture. The authors claimed that reactions 2.55, 2.56 and 2.58 will occur consequently. H_2 gas formation can be confirmed by the oxidation peak of H_2 gas applied separately in a different experiment on the same molten salt composition and temperature at 1 atm (White and Twardoch 1983). From the cyclic voltammograms (CVs) shown in Figure 2.14, two small cathodic peaks were observed before the main reduction peak using a 200 V/s scan rate and three different CO_2 partial pressures (P_{CO_2}) of 185.7, 37.1 and 7.4 mm Hg at 17.1 mm Hg of H_2O partial pressure (White and Twardoch 1984).

In this case, the pre-reduction peak in the case of $P_{\text{CO}_2} = 7.4\text{ mm Hg}$ and the 200 V/s scan rate was attributed to hydrogen adsorption after the reduction of the bicarbonate ion to hydrogen atoms via reaction 2.56. The product of the main reduction peak (X) shown in Figure 2.14 was not reported.

The reduction of gases at this cathodic pre-peak in pure CO_2 (without H_2O) was reported by Lantelme, Kaplan et al. (1999). It was suggested that some gases are adsorbed on the surface of the cathode at a cathodic peak of -0.45 V as shown in Figure 2.15.

However, the last peak was also found in other CV investigations on the gold electrode at 1 bar pressure of CO_2 in two binary molten carbonates: Li_2CO_3 - Na_2CO_3 (52-48 %mol) at $600\text{ }^{\circ}\text{C}$ and Li_2CO_3 - K_2CO_3 (62-38 mol%) at $575\text{ }^{\circ}\text{C}$.

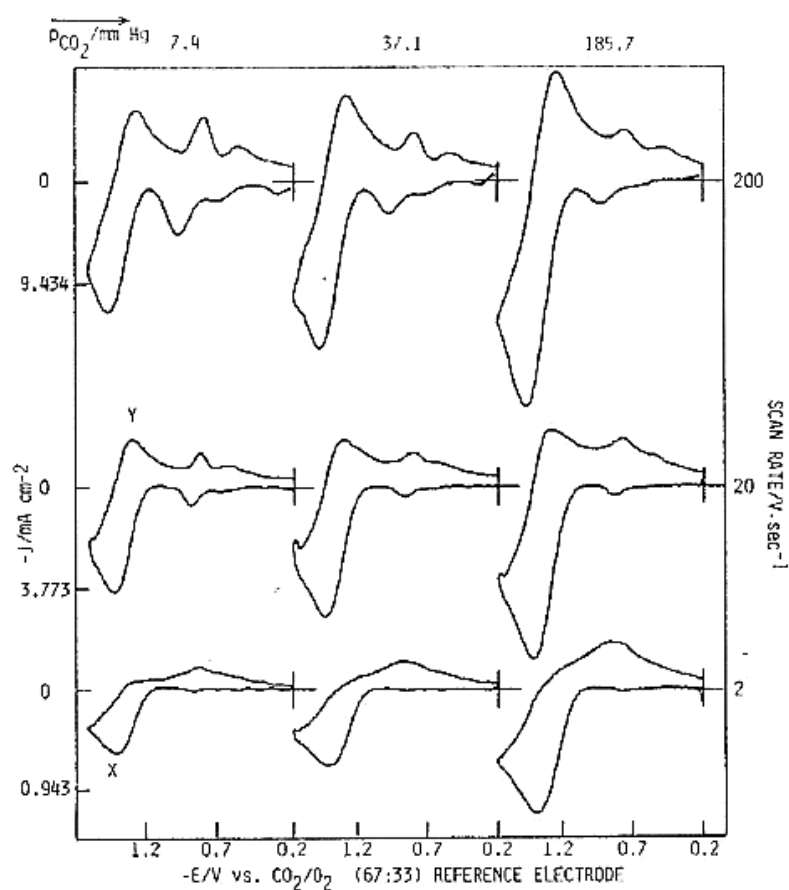


Figure 2.14. Cyclic voltammogram obtained on a gold electrode at three different scan rates under a partial pressure of 17.1 mm Hg for water, and different partial pressures for carbon dioxide and argon (<25% CO₂) (White and Twardoch 1984).

It can be seen that the reduction potential of CO₂ in the (Li/Na) carbonates as presented by peak 1 in Figure 2.16 at 100 mV/s, for instance, was more negative than the potential obtained in the case of the (Li/K) carbonates, i.e. peak 2 in Figure 2.17 at the same scan rate versus the Ag⁺/Ag reference electrode. Peak 1 in the (Li/K) carbonate case shown in Figure 2.17 was assigned as a pre-peak for the reduction of CO₂ to CO₂²⁻.



This pre-peak was investigated also in the molten chloride in the absence of Li^+ ions as will be illustrated in the next section.

The performance of the three types of molten carbonates was compared at the equivalent temperature of 600 °C:

1. Li_2CO_3 - K_2CO_3 (62-38 mol%) (Li/K).
2. Li_2CO_3 - Na_2CO_3 (52-48 mol%) (Li/Na).
3. Li_2CO_3 - Na_2CO_3 - K_2CO_3 (43.5, 31.5, 25.0 mol%) (Li/Na/K).

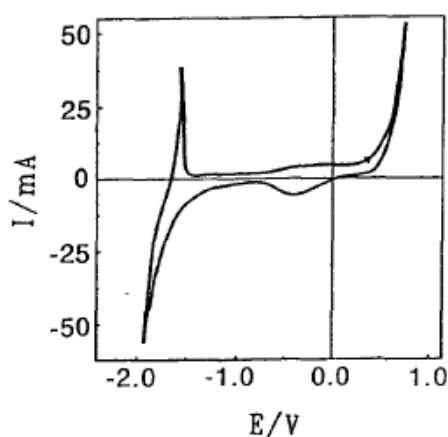


Figure 2.15. Cyclic Voltammogram acquired from a gold electrode with 0.33 cm^2 in surface area in Li_2CO_3 - Na_2CO_3 - K_2CO_3 ; the potential scan rate: 1 V s^{-1} . Temperature: 450 °C. Reference: CO_2 - O_2 (Lantelme, Kaplan et al. 1999).

It has been observed that besides its lower melting point, the eutectic mixture (3) has unique characteristics such as higher solubility for CO_2 (Kanai, Fukunaga et al. 2013) and a high exchange current value in fuel cells (Ang and Sammells 1980). Moreover, the ternary eutectic salt has basically more particles of alkali metal salts than other eutectic mixtures (1,2) and the

particles are consequently closer in the coordination, decreasing the transferrable capability of oxygen ions O^{2-} in the salt. This feature is preferred for increasing the feasibility of the partial oxidation of CH_4 produced primarily at the cathode. This in turn hinders the possible oxidation of the fuel to CO_2 and H_2O (Ao, Wang et al. 2008).

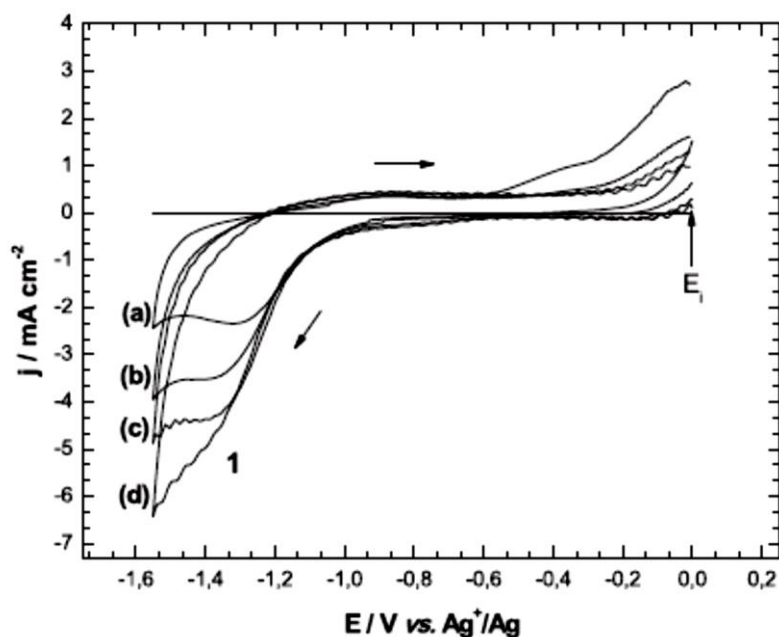


Figure 2.16. Cyclic voltammogram of a gold electrode in Li_2CO_3 - Na_2CO_3 (52-48 mol%) at 600 °C under $P_{CO_2}=1$ bar. Potential scan rates: (a) 50 $mV s^{-1}$ (b) 100 $mV s^{-1}$ (c) 200 $mV s^{-1}$ (d) 300 $mV s^{-1}$, $E_i=0$ V versus Ag^+/Ag reference electrode (Chery, Albin et al. 2014).

Actually, both Li_2CO_3 and K_2CO_3 add a unique characteristic to the overall eutectic salt properties. Li_2CO_3 in the molten salt can lower the melting point of the mixture and enhance the process of carbon deposition, although it requires higher energy for CO_2 reduction (Chery, Albin et al. 2014). Whereas a small amount of K_2CO_3 in the molten salt composition increases its melting

point but offers lower energy consumption for the reduction process as illustrated above.

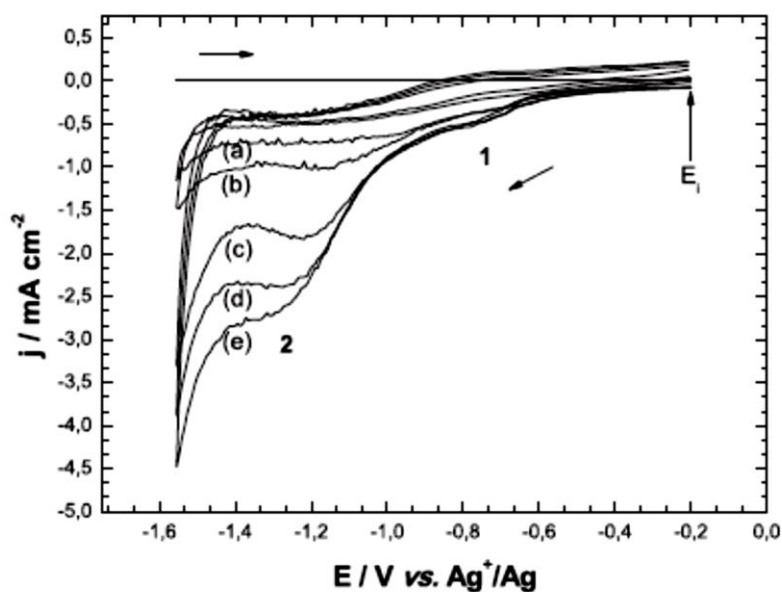


Figure 2.17. Cyclic voltammogram of a gold electrode in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (62-38 mol%) at 575 °C under $P_{\text{CO}_2}=1$ bar. Potential scan rates: (a) 10 mV s^{-1} (b) 20 mV s^{-1} (c) 100 mV s^{-1} (d) 150 mV s^{-1} (e) 200 mV s^{-1} , $E_i=0 \text{ V}$ versus Ag^+/Ag reference electrode (Chery, Albin et al. 2014).

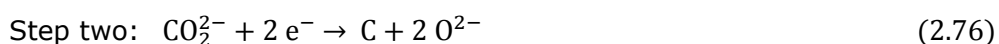
2.3.1.2. Molten chloride salts.

The adsorption of hydrogen atoms on the platinum electrode has been observed also in the LiCl-KCl eutectic mixture at 450 °C during the investigation of the influence of water on the molten chloride (Kanzaki and Takahashi 1975). Reaction (2.57) was suggested in this regard to elucidate the process.

By the same mechanism mentioned previously, another H atom can be formed and the two H atoms can be dimerised to H₂ according to reaction (2.33) (White and Twardoch 1987).

However, carbonate ions can be added to the molten chloride salt for use as carbonate ions in CO₂ reduction at lower melting points. The influence of the carbonate ion can be seen when just 1% mol of K₂CO₃ was added for instance to LiCl-KCl molten salt at 500°C (Song, Xu et al. 2012). In the case of clear molten chloride under an argon gas atmosphere, a significant cathodic current peak was observed on the CV of a graphite electrode at -3.5 V due to the reduction of lithium chloride to lithium metal (C1) in Figure (2.18a). However when 1 mol% of K₂CO₃ was added, the starting potential of peak C2 had a positive shift compared to C1, suggesting that carbon was deposited first before lithium intercalation during the course of recording the CV in the molten mixture of LiCl-KCl-1%K₂CO₃. Carbon deposition can be confirmed then by the oxidation peak (A3) observed in the reverse scan and separated from peak A2 representing lithium extraction in Figure (2.18b).

The reduction of CO₂ to carbon was also investigated in the KCl-NaCl eutectic mixture at 700 °C with or without adding Li₂CO₃ under the pressure of CO₂ gas (Halman and Zuckerman 1987). The findings suggest the following steps in the absence of Li₂CO₃:



The detection of CH₄ traces in the cathodic gas product was also observed in molten chloride (Halman and Zuckerman 1987). The investigation assigned the presence of CH₄ to the moisture associated the CO₂ gas when applied to

the electrolysis of LiCl-KCl (58.5:41.5 mol%) without carbonate formation. This is similar to the mechanism mentioned in the molten carbonate section.

Generally, H_2O can interact with molten chlorides generating hydrogen chloride (HCl) especially at temperatures higher than 425°C and water vapour pressures greater than 20 mm Hg (White and Twardoch 1984; Chen and Fray 2002)



Or,

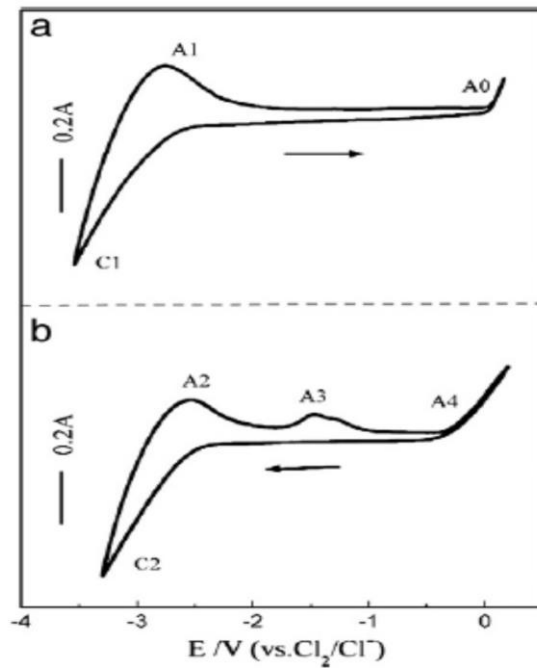


Figure 2.18: Cyclic voltammograms obtained on a graphite electrode in LiCl-KCl melts (a) without K_2CO_3 (b) with 1 mol% K_2CO_3 . The scan rate is: 50 mV/s (Song, Xu et al. 2012).

It is worth noting that CO_2 can react with O^{2-} or OH^- ions (generated from reactions 2.77, 2.78) to produce carbonate ions according to reaction (2.59) or (2.83) respectively (Kamali and Fray 2015). The carbonate ions can then be electro-reduced in turn to carbon or CO.

2.3.1.3. Molten hydroxides.

The most effective reasons for using molten hydroxides in electrosynthesis are the high ionic and thermal conductivity, and the low melting point of the eutectic melt (200-400 °C). The melting point of NaOH for example is 318 °C. Molten hydroxides have been also used in extractive metallurgy to reduce iron oxide (Fe_2O_3) to iron metal for instance in molten NaOH at 530 °C (Cox and Fray 2008).

Generally, molten hydroxides can behave like H_2O does during acid-base dissociation as follows (Glibert 1983):



Here, H_2O and O^{2-} represent the conjugate acid and base respectively, and the use of pH_2O as $(-\log[\text{H}_2\text{O}])$ in the electrochemical system is exactly analogous with the use of pH in the aqueous solution. The hydroxide ion can either accept a proton (H^+) to produce a water molecule or detach a proton to yield an oxide ion (Lovering and Gale 1983):



As a result, H_2O will be the strongest acid and the O^{2-} ion will be the strongest base (according to the Bronsted theory) that can be found in the melt. Also, in

the event of the expense of the H_2O content, the O^{2-} concentration may increase as well. According to the Pourbaix diagram shown in Figure 2.19 based on Tremillon's work, H_2 can be produced in an acidic melt ($\text{pH}_2\text{O}=0$ or less) at greater reduction potentials (less positive) than +0.8 V versus the normal sodium electrode (Tremillon 1966) (reaction 2.68).

For less acidic media, H_2 should be produced at even more negative potentials or at a higher energy required for electrolysis. It can be seen from Figure 2.19 also that peroxide and superoxide ions can be generated on the anode besides O_2 in the case of low acidity ($\text{pH}_2\text{O}>0$).

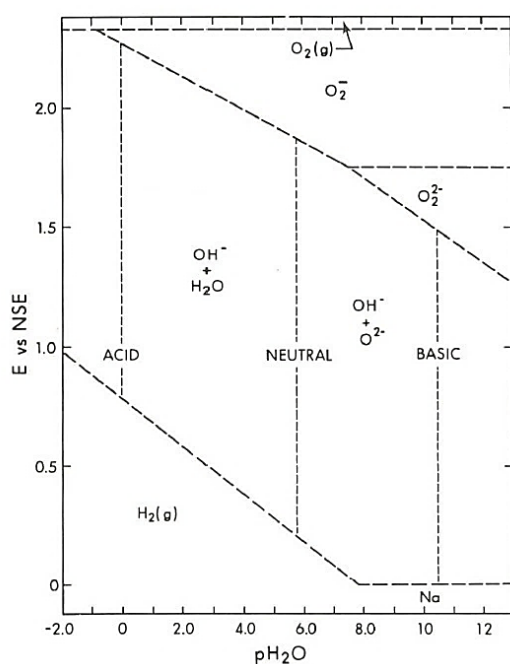


Figure 2.19. The potential-oxoacidity (E - pH_2O) diagram for the molten hydroxide at 500°K (226.8 °C) showing O_2 and H_2 gas potentials versus the normal sodium electrode (Tremillon 1966).

From the voltammetric study, H₂ gas is generated from the reduction of H₂O using the platinum electrode in the NaOH-KOH molten salt at 220 °C according to reaction 2.25.

However, when recording the CV on a rotating nickel disc electrode in molten NaOH containing 0.42 wt% H₂O at 350 °C, sodium as an alkali metal was deposited at a potential more negative than -2.0 V versus (Ni/NiO) (Divisek, Mergel et al. 1980) according to the following reaction:



Sodium metal obviously is not preferred as a product during electrolysis, and this is in agreement with the need for higher energy consumption for sodium deposition.

Nevertheless, the reduction of CO₂ to CO or carbon via any mechanism in a molten hydroxide has not been discovered yet. The lack of interest was justified due to the reactivity of CO₂ with a molten hydroxide in general, thereby releasing carbonate ions (Zecevic, Patton et al. 2004):



It has been stated that carbonate ions are electrochemically inactive inside molten hydroxides (Plambeck 1976). Moreover, CO₃²⁻ ions will result in a further increase in the melting point of the entire eutectic salt. However, hydroxides can be introduced in the composition of molten carbonates to increase the opportunity of fuel or hydrocarbon formation in particular from the direct electrolysis of the molten salt as stated before in section (2.2).

Both mixtures of NaOH-KOH (50:50 mol%) and LiOH-NaOH (27:73 mol%) have been used commonly in the literature. The addition of lithium hydroxide

to the NaOH-KOH mixture does not lower the melting point significantly. Therefore, the ternary molten mixture of NaOH-KOH-LiOH has not been employed.

2.3.1.4 Molten nitrate salts

Molten nitrates have been used widely in electrochemistry. Two binary mixtures of molten nitrate were actually concluded; LiNO₃-KNO₃ with 43:57 mol% and a melting point of 132 °C; and NaNO₃-KNO₃ with 50:50 mol% that has a melting point of 228 °C. The ternary molten nitrate (LiNO₃-NaNO₃-KNO₃) with 30-17-53 mol% does not have any temperature advantage over the LiNO₃-KNO₃ salt as the former mixture melts at 125 °C.

The binary equimolar mixture of NaNO₃-KNO₃ is preferred as it is more thermally stable than LiNO₃-KNO₃.

Working with molten nitrates as oxidising compounds can be risky particularly at high temperatures (over 500 °C). Due to their low melting point though, molten nitrate can be used in metal modification as stated before, having the property for avoiding the rapid thermal decomposition incurred when using other types of molten salts. Also, it was used effectively in the nitration of organic compounds in order to produce solvents, dyestuffs, pharmaceuticals and explosives in addition to the formation of intermediate products for the preparation of other compounds like amines.

It has been confirmed that H₂O can be co-reduced simultaneously with nitrate ions at 230 °C under a partial pressure of water vapour of 10 mm Hg, producing both nitrite and hydroxide ions:



There was little confirmation though about the direct formation of atomic hydrogen (H) by the one-electron transfer reduction of H₂O with the generation of NO₂ gas according to reaction (2.57).

Then the following reactions can occur:



Or,



CO₂ can behave like H₂O and be co-reduced along with the nitrate anion into carbonate ions in the melt.



This reduction has been described as massive due to the irreversibility and the high rate of the reaction.

Regarding the oxidation reaction, it was stated in the case of water vapour application (for instance), that two anodic voltammetric waves can be seen that are assigned to the formation of oxygen (O₂) and NO₂ gas respectively:



Therefore, it can be concluded from the above description that the applied voltage required to drive the reduction of CO₂ and water vapour in molten nitrate, will lead to the rapid formation of carbonate ions and NO₂ gas with a minor amount of hydrogen gas.

2.3.2. Effect of temperature

As reported in the literature, many researchers performed voltammetric experiments at fixed temperatures to study the effect of other parameters like the changes to applied cell voltage or CO₂/H₂O ratio. In the same salt mixture, it is agreed that temperature has a minor effect on carbon deposition according to Kaplan, Groult et al. (2002). However, CO can also be detected at temperatures higher than 775 °C (Lorenz and Janz 1970). CO seems to be the dominant product at 900 °C or above when CO₂ is reduced in the absence of water (Kaplan, Wachtel et al. 2010). In addition to the electro-reduction of CO₂ to CO, the following chemical reaction can take place:



Although CO₂ reduction to carbon is thermodynamically favoured, CO is clearly identified at temperatures higher than 800 °C when reaction 2.89 will be deemed feasible (i.e. $\Delta_r G$ starts to be negative). As a sequence, the electrical efficiency of CO formation will be higher than that of carbon deposition. Apart from carbon formation, reactions (2.1, 2.2) seem to be generally more feasible at higher temperatures based on thermodynamic data as the entropy change ($\Delta_r S$) of CO₂ and H₂O individual dissociation (to CO and H₂) is high at increasing temperatures, decreasing the $\Delta_r G$ value in turn (Figure 2.2) (Chery, Lair et al. 2015).

This basically means that the electrolysis of both CO₂ and H₂O will be preferred at higher temperature levels. However, CO₂ reduction will consume higher energy than water reduction up to 820 °C (Chery, Lair et al. 2015).

In the presence of water, Busson, Palous et al. (1967) found the evolution of H₂ gas besides CO in ternary molten carbonates even at temperatures higher

than 600 °C due to the prospective effect of the WGS reaction (reaction 2.41) as stated previously.

2.3.3 Effect of applied electrolysis voltage

The use of an appropriate applied voltage is very important. As reported previously, the formation of carbon is favoured at potentials more negative than -1.9 V vs. CO₂-O₂ electrode in ternary molten carbonates at 450 °C (Figure 2.15). Using potential values more negative than this limit in electrolysis results in the formation of CO gas in addition to carbon deposition (Lorenz and Janz 1970; Ijije, Lawrence et al. 2014). Applying cell voltages higher than this limit during electrolysis may result in alkali metal deposition (M) (reaction 2.74) and result in indirect chemical reduction of carbonate ions (Ijije, Lawrence et al. 2014):



However, H₂ gas can be detected at less negative potentials (-0.6 to -0.95V) vs. the CO₂-O₂ reference electrode, depending on the CO₂ concentration in the inlet gas (Figure 2.14) (White and Twardoch 1984). Lantelme, Kaplan et al. (1999) suggested that some gases were produced at less negative potentials than the main reduction cathodic peak as shown in Figure 2.15. However, the composition of these gases is not explained.

Thus it can be seen that H₂ production is very sensitive to the change in applied voltage during electrolysis in terms of providing sufficient energy for carbon deposition or even CO. This behaviour can positively or negatively affect hydrocarbon formation and should be addressed in future studies.

2.3.4 Effect of the CO₂/H₂O ratio

In reality, the ratio of CO₂/H₂O and its variations have been rarely studied in molten salt chemistry, particularly using electrochemistry. It has been taken into consideration in this research due to the effect of CO₂ and H₂O concentrations on electrolysis in molten salts. In the case of carbonate molten salts, changing water composition in the feed gas mixture of CO₂-H₂O at a relatively low CO₂ concentration (<25% vol. of feed gas) plays a major role in H₂ gas evolution as shown in Figure 2.14 (White and Twardoch 1984). H₂ evolution peaks were found more clearly by high current density on CVs performed at the lowest value of CO₂ partial pressure of 7.4 mm Hg. There was no evidence actually about the effect of water composition at higher CO₂ concentrations (>75%vol. of feed gas) as shown in Figure 2.20 below.

The effect of excess H₂O can result in higher levels of H₂ content due to the water gas shift reaction (2.41) as the CO resulting from the electrolysis at high temperatures can transform to H₂, thereby increasing the H₂/CO ratio in the product. Furthermore, the solubility of H₂O and CO₂ is provided at different values for various molten salt types and compositions. Subsequently, water can demonstrate a more significant effect than CO₂ for some molten salts (White and Twardoch 1983).

It can be seen also from both Figures (2.14 and 2.20) that the main cathodic peaks marked with 'X' increase with CO₂ partial pressures in both cases (of high and low CO₂ concentrations) as the current density increases with increasing CO₂ partial pressure. In brief, rising P_{CO_2} increases the amount of dissolved CO₂ in the melt and consequently the amount of CO formed by CO₂ reduction (reaction 2.44 or 2.72) (Chery, Albin et al. 2016).

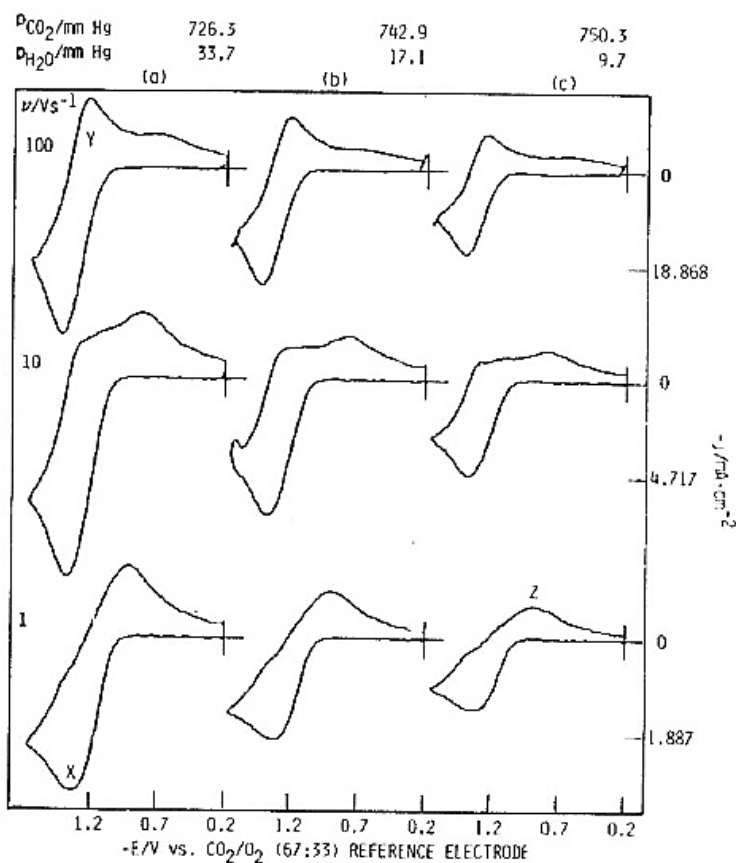


Figure 2.20. Cyclic voltammogram obtained at three different scan rates on a gold electrode in a ternary carbonate melt at 460 °C. The composition of the atmosphere was (a) $p\text{CO}_2=726.3$ mm; $p\text{H}_2\text{O}=33.7$ mm, (b) $p\text{CO}_2=742.9$ mm; $p\text{H}_2\text{O}=17.1$ mm; (c) $p\text{CO}_2=750.3$ mm; $p\text{H}_2\text{O}=9.7$ mm. (White and Twardoch 1984)

2.3.5 Effect of the catalyst

As mentioned previously, molten salts themselves can act as catalysts to promote the formation of hydrocarbons from the partial oxidation of CH_4 for example, due to the role of peroxide (O_2^{2-}) and superoxide (O^-) ions in the molten salt. The term 'catalyst' here is utilised actually to see the influence of

various metals or metal oxides as inert electrodes or additives inside molten salts and how they catalyse the process of electrolysis in general.

At higher temperatures ($>800\text{ }^{\circ}\text{C}$), valve metals (Ta, Nb, Zr, Al, Ti, Hf, W) have been mostly studied as candidate materials to promote the reduction of CO_2 to CO due to their stability at elevated temperatures and the formation of an oxide layer outside the metal surface (which is more conductive at higher temperatures than at lower temperatures), promoting in turn electrolysis (Kaplan, Wachtel et al. 2010). Amongst these metals, Ti has been deemed as the most appropriate metal because it does not combine with Li ions when Li_2CO_3 was used as a single molten salt; additionally TiO_2 can also be insoluble at $900\text{ }^{\circ}\text{C}$ (Chauvaut and Cassir 1999).

At lower temperatures, carbon fibres (nanostructure) in the form of a different kind of carbon, were obtained from the reduction of ternary carbonate molten salts at $450\text{ }^{\circ}\text{C}$ using nickel as the cathode material (Kaplan, Groult et al. 2001). However, precautions must be taken when using nickel as an anode due to its oxidation to NiO which is an insulator that acts against electrolysis (Lantelme, Kaplan et al. 1999).

2.4. Summary

This chapter began with a description of the techniques employed for CO_2 conversion using H_2O to give valuable materials such as H_2 , CO and various hydrocarbons. The techniques include CO_2 and H_2O dissociation by metal oxide thermochemical cycles and electrolysis by the reduction of CO_2 and H_2O to fuels. The electrolysis itself was divided into two categories: low temperature and high temperature electrolysis. Through low temperature electrolysis, CO_2 and H_2O can be co-reduced directly to hydrocarbon species such as CH_4 , C_2H_4 , C_2H_6

and HCOOH in addition to H₂ and CO. However, the hydrocarbon production rates would reduce quickly on the cathode in this case because of side reactions of H₂ and CO formation as a result of the proximity of CO₂ and H₂O reduction potentials, particularly for aqueous solutions. Performing electrolysis at high temperatures (200-600 °C) can yield both thermodynamic and reaction rate advantages. CO₂ and H₂O can be reduced to CO and H₂ respectively in the solid oxide cell at (850-950 °C), achieving a high current efficiency of up to 100%. O₂ gas can be produced effectively on the anode. However, in addition to cell degradation (electrode sintering and agglomeration) at high temperatures, an additional step is required to feasibly obtain hydrocarbons at lower temperatures (200-500 °C) through the Fischer-Tropsch process (reaction 2.5). The latter is aided with a catalyst to form alkane hydrocarbons (C_nH_{2n+2}) for instance.

Alternately, molten salts can work as ionic liquids at higher temperatures (200-600 °C) to perform reduction effectively into carbon, CO and H₂.

From the available and relevant literature, hydrocarbon formation in general has not been confirmed directly from the electrolysis of CO₂ and H₂O in molten salts. In one of the recent investigations though, long-chain hydrocarbon species (such as C₂H₄, C₃H₆ and C₄H₈) were found in the cathodic product beside H₂, CO and CH₄ during the electrolysis conducted in molten salt carbonate-hydroxide mixture at 450 °C and 2.5 V. Nevertheless, the formation of CH₄ has been justified due to the reaction of H₂ with carbon or CO during the electrolysis of wet CO₂ in ternary molten carbonate mixtures at temperatures below 500 °C.

If CO₂ is diluted with Ar prior to electrolysis, CH₄ can be oxidised partially to a methyl radical by the activity of superoxides (O⁻ and O₂²⁻) produced through

the transitions of O_2 and oxide ions (O^{2-}) in the molten salt at temperatures between 500-800 °C.

Under the same conditions as the molten salt above, methyl radicals can be transformed to various kinds of hydrocarbons through the alkylation or polymerisation process at 500 °C. Also, adsorbed atomic hydrogen and carbon (both produced from CO_2 and H_2O co-reduction in molten salts) can react together to produce hydrocarbons up to C_3 species.

Apart from molten carbonates, hydrocarbon species including CH_4 have not been discovered in molten hydroxides or chlorides.

From the literature reviewed, the effect of temperature was studied in molten carbonates. It was found that CO can be the predominant product above 800 °C in the absence of water. Alternately, H_2 can be produced even at temperatures higher than 800 °C according to the water gas shift reaction. The higher applied voltage than required for CO or carbon production can result in alkali metal deposition with a greater consumption of energy according to several authors.

Chapter 3

Methodology

3.1 Equipment, materials and chemicals

The chemicals used in the research are listed in Table 3.1. Materials used for crucibles, ceramic tubes, electrodes etc. are listed in Table 3.2. Equipment that employed to carry out the electrolysis, cyclic voltammetry and gas analysis are listed also in Table 3.2.

Table 3.1 – Chemicals (and their suppliers information) used in this research

Chemical	Chemical Formula	Supplier	Details
Lithium carbonate	Li_2CO_3	Sigma Aldrich	Purum grade, $\geq 99.0\%$
Sodium carbonate	Na_2CO_3	"	ACS reagent grade, $\geq 99.5\%$
Potassium carbonate	K_2CO_3	"	ACS reagent grade, $\geq 99.0\%$
Lithium Chloride	LiCl	"	99%
Potassium Chloride	KCl	"	$>99.9\%$
Lithium hydroxide	LiOH	"	Reagent grade, $\geq 98\%$ powder
Sodium hydroxide	NaOH	"	Reagent grade, $\geq 98\%$ pellets
Potassium hydroxide	KOH	"	Reagent grade, 90% flakes
Carbon dioxide	CO_2	Air products	99.99%
Argon	Ar	"	99.99%
Water	H_2O	Millipore corporation	Millipore grade
Labovac 10 mineral oil	-	Jencons	-

Table 3.2 Materials and equipment (and their suppliers information) used in this research

Materials and equipments	Model/Grade	Supplier
For hydrocarbon production		
Vecstar tube furnace	150 mm bore, maximum temperature of 1100 °C and 2416CG Eurotherm programmable PID 8 segment controller	Vecstar Furnace Ltd.
Alumina crucible	(1) 92mm outer diameter, 85mm inner diameter, 100mm height. (2) 80mm outer diameter, 73mm inner diameter, 85mm height.	Almath Crucibles Ltd.
Alumina tubes	(1) Two of 38mm outer diameter, 32mm inner diameter, 500mm height. (2) Two of 25mm outer diameter, 19.5mm inner diameter, 500mm height	Almath Crucibles Ltd.
Silicon rubber bungs	-	Fisher scientific
Silver wire (1 mm)	99.99% pure	Advent Research Materials
Stainless steel rod (6 mm diameter)	304 (18% Cr, 8% Ni and 2% Mn)	Unicorn Metals
Mild steel rod (5 mm diameter)	BDMS(0.16% C, 0.4% Si and 0.7% Mn)	"
Titanium foil (1 mm thickness)	99.9% pure	Good fellow Cambridge Ltd.
DC power supply	E3633A (20 A, 10 V)	Agilent
Potentiostat	Autolab PGSTAT30	Ecochemie

Table 3.2 (continued ..)

For gas analysis		
Materials and equipments	Model/Grade	Supplier
Gas chromatography	Clarus 480 GC	PerkinElmer
Mass spectrometry-gas chromatography	JEOL AccuTOF GCX	JEOL Ltd., Tokyo, Japan
Gas detector tubes	Gastec	a1-cbiss

3.2 Set up of electrochemical molten salt reactor

In this research, a cylindrical retort was built in house with a flange type cover using the 316-grade stainless steel (17% Ni, 12% Cr, and 2% Mo) to shape the reactor to provide and control the environment needed for the molten salt electrolysis as shown in Figure 3.1. The dimensions of the retort were 130 mm internal diameter, 7.5 mm wall thickness and 800 mm vertical length. A cooling water jacket (Height: 65 mm; Diameter: 200 mm; Thickness: 10 mm) was manually welded to the retort with the flange as illustrated in Figure 3.2. On the flange cover, there were some holes drilled for the insertion of ceramic tubes (used for anode and cathode gas collection), observation purposes and sealing.

The retort was placed through the bore of a custom-built vertical tube furnace (Vecstar Furnaces Ltd.) of 160 mm internal diameter and 500 mm tube length. A 2416CG Eurotherm programmable PID 8 segment controller was employed to control the furnace whose maximum working temperature was set at 1100 °C with an accuracy of ± 1 °C. The retort was inserted centrally in the furnace. The gap between the retort wall and the bore of the furnace was covered with an alumina board (ZIRCAR Ceramics) on the top of the furnace to reduce heat losses as shown in Figure 3.1. A rubber gasket was used to seal the retort

between the lid (flange cover) and the body over the water cooling water jacket. Two silicon rubber bungs (Fisher Scientific Ltd.) served to hold the electrodes inside the ceramic tubes while two more holes have been placed inside each bung to collect the cathodic and anodic gases from each tube. Two small bungs else though were used also to seal the observation holes. The ceramic tubes themselves were sealed through the lid by two individual filter adapters (Fisher Scientific Ltd.). Therefore, the tubes served actually for both holding electrodes and gas product outlets. The cooling water jacket functioned to cool the upper part of the retort ensuring the safe handling and avoiding the prospect overheating or melting of the silicon bungs (and adapters). Another hole in the retort lid was used to insert a smaller ceramic tube (ID) for gas feed inlet sealed from the retort by a silicon rubber bung. This tube was long enough to reach just above the surface of the molten salt contained in an alumina crucible.

CO₂ (99.99%) and Ar (99.99%) were supplied by Air Products Ltd. in the respective cylinders. The cylinders were each fitted with a 2-stage gas regulators (GIS Leengate). The outlets of the two gas cylinders were set to 0.12 MPa and connected to rotameters (Roxspur Measurement and control) of the flowrate ranges from 20 to 200 mL/min and from 5 to 100 mL/min at ambient temperature and pressure (ATP) for CO₂ and Ar respectively. After leaving the flowmeters, CO₂ and Ar were mixed together before introducing to a dreschel bottle containing 100 mL Millipore grade deionised water to obtain the desirable content of steam (water vapour) in the gas inlet of the reactor. The outlet gas tube from the reactor shown in Figure 3.1 was connected to another dreschel bottle containing Labovac 10 mineral oil (Jencons) to prevent air entry into the reactor (Figure 3.3). A stopcock valve was fitted in the way from the reactor gas outlet to the dreschel bottle when it was necessary to

close the gas outlet during the electrolysis. In the retort, a stainless steel stand (Height; 380 mm) was placed and a refractory brick was mounted on it as shown in Figure 3.3. An alumina crucible (Almath) containing the molten salt was sat on the brick in the furnace. The described design was modified actually from the previous experiments of molten salt electrolysis in high temperature laboratory (Ijije 2015).

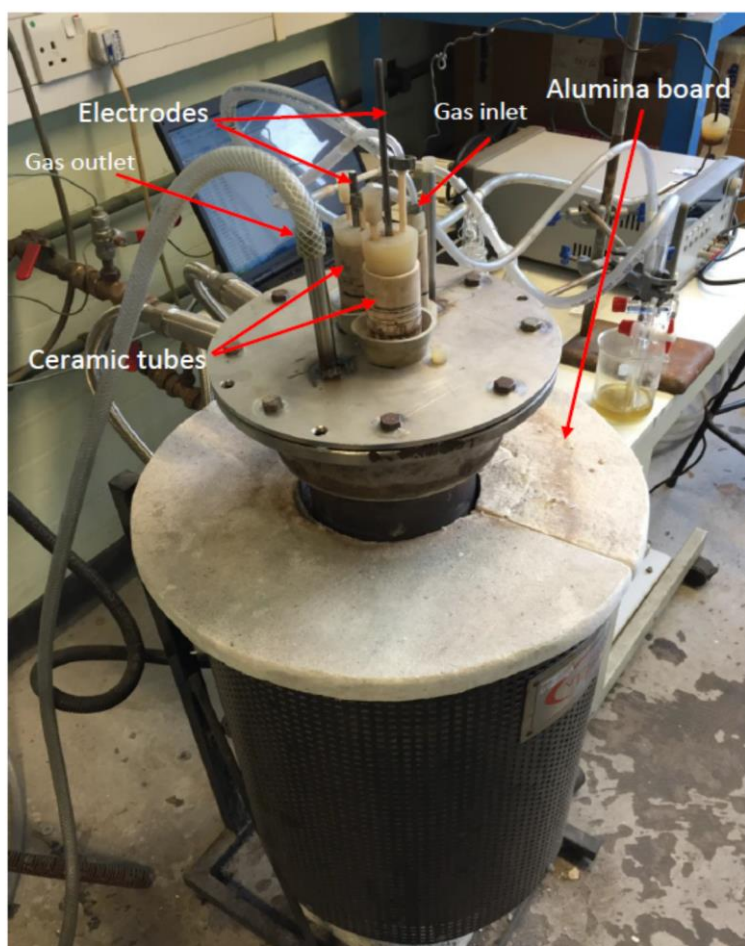


Figure 3.1. Full experiment setup for molten salt reactor in the laboratory.



Figure 3.2. The retort placed in a tube furnace

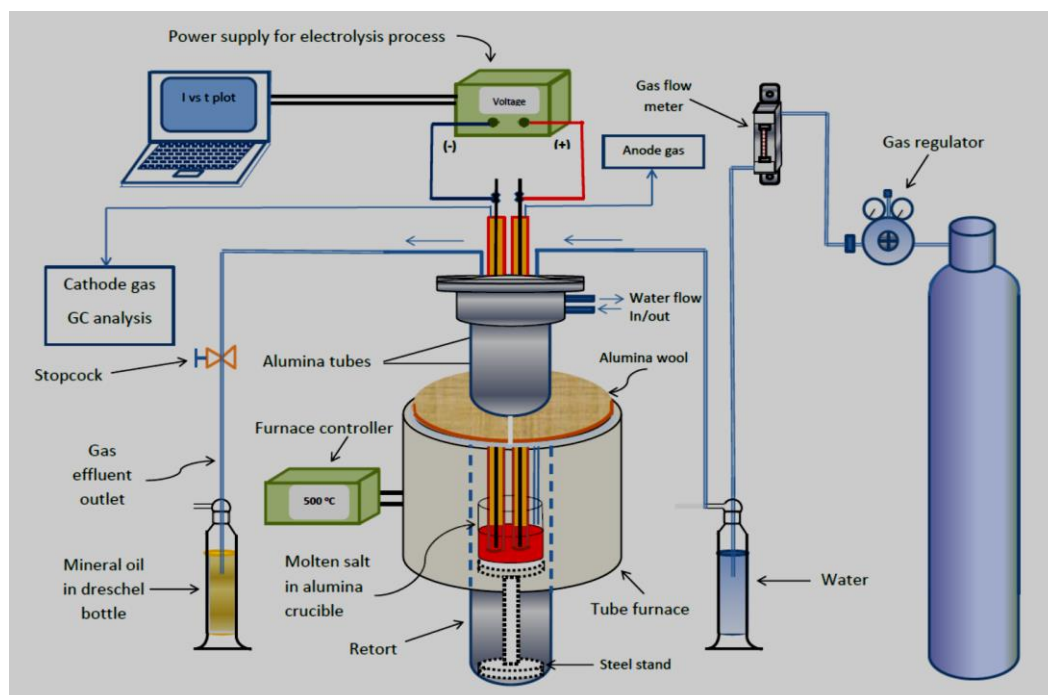


Figure 3.3: A schematic diagram of the experimental setup for electrolysis.
(modified from (Ijije 2015))

Before the beginning of the experiment, the mixed gases was set to the required flow rate, and the furnace temperature was increased gradually in intervals of 200 °C until achieving the desired temperature. To measure the temperature inside the molten, a YCT-727D thermometer (TC Direct) was employed in the experiment attached with a Type K 1 m long thermocouple (3 mm diameter, 310-grade stainless steel). The insulated thermocouple was put in the molten salt for approximately 1 to 2 minutes to obtain an accurate and stable measurement.

It is assumed that the furnace gave a symmetric temperature profile to the crucible containing molten salts. Therefore, the temperature itself has been considered as constant during the experiments and the thermocouple was not fitted in the reactor. However, the temperature fluctuation could be significant during the electrolysis. This is actually one of the technical limitations in the research.

The two electrode tube gas outlets were each connected to another dreschel bottle containing the mineral oil to observe the outlet gases produced and reduce electrolyte contamination. Gas product samples were collected using a tedler 1 L (SKC Ltd.) gas bag via a connection from the cathodic gas tube.

3.3 Electrolytes used in the research

In this work, four combinations of molten salts were used as electrolytes: a mixture of molten carbonates ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$), a mixture of molten chlorides (LiCl-KCl) and two mixtures of molten hydroxides (LiOH-NaOH and KOH-NaOH). For the salt mixtures, eutectic compositions were chosen from the thermodynamic phase diagrams shown in Figure 2.9b for ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$) and Figures 3.4a-c for the other salts.

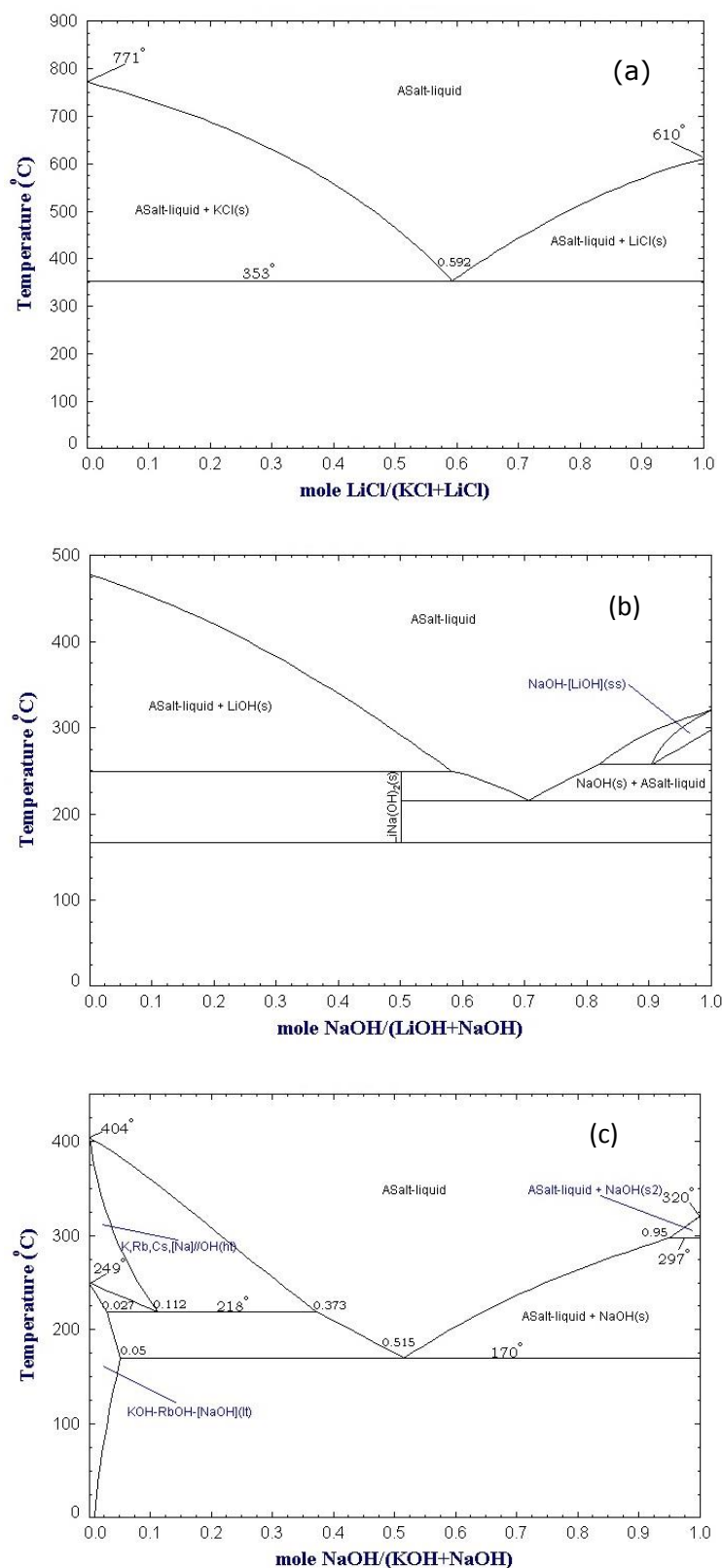


Figure 3.4: Phase diagram in mole percentages for (a) binary chloride (LiCl-KCl) salt (b) binary hydroxide (LiOH-NaOH) and (c) binary hydroxide (KOH-NaOH) (FACILITY FOR THE ANALYSIS OF CHEMICAL THERMODYNAMICS 2012)

The different salt compositions used and their particular eutectic melting temperatures are given in Table 3.3

Table 3.3- Electrolyte compositions and eutectic melting temperatures used in this research. (Janz 1967)

Electrolyte	Composition (Molar ratio)	Eutectic melting temperature (°C)
Li ₂ CO ₃ -Na ₂ CO ₃ -K ₂ CO ₃	43.5:31.5:25	397
LiCl-KCl	58.5:41.5	361
LiOH-NaOH	27:73	218
KOH-NaOH	50:50	170

In general, the key point of choosing the appropriate molten salt is the ability to work at an operating temperature, as low as possible, maintaining the liquid state to enable the electrolysis and promote hydrocarbon formation.

3.4 Electrodes used for molten salt experiments

3.4.1 Working electrode/cathode material

In the three electrode cell (explained later in the next section), a silver wire (1 mm in diameter) was used for studying molten hydroxides, while a graphite rod of 5 mm in diameter was used in molten chlorides. The silver wire and graphite rod were chosen because of their good resistivity to the attack of hydroxide and chloride ions, respectively. To reduce the cost, a 100 mm long of silver wire was attached to a polished stainless rod (1 mm diameter and 400 mm long) using a 0.25 mm diameter thick stainless steel wire. The stainless steel rod was then held inside the retort through the lid using a silicone rubber

bung. For the quite same reason, a 100 mm long graphite rod was drilled and a mild steel rod (BDMS, 5 mm diameter) was screwed inside the graphite. For experiments in the two electrode cell, a mild steel rod (BDMS, 5 mm diameter) was used as the cathode in both carbonate and hydroxide molten salts whereas the same graphite rod mentioned above was employed in molten chlorides as the cathode. A nickel rod of 5 mm diameter and titanium foil of (25*100*1 mm) dimension were used also as cathode materials in molten carbonate to see the selective production of hydrocarbon species. A titanium foil of (25*100*1 mm) was also used as the cathode and connected to the mild steel rod and tied using the stainless steel thick wire as mentioned above.

3.4.2 Counter electrode/ anode material

A 6 mm diameter stainless steel rod (304 grade) was used in the case of both molten carbonate and hydroxide as the counter electrode or anode. The stainless steel exhibits sufficiently good oxidation resistivity and conductivity in addition to its moderate cost. In the case of molten chloride, the counter electrode/anode material was graphite rather than stainless steel because of the relatively high oxidation activity of most of transition metals such as Fe, Ni, Co, etc. inside molten chloride.

3.4.3 Reference electrode

Cyclic voltammograms were recorded in the three-electrode cell in which the reference electrode has to be inserted so that the working electrode potential can be monitored and controlled considering a constant potential of the reference electrode. The potentiostat allows only a negligible current to pass through the reference electrode and its potential remains unchanged on a practical and analytical point of view. Reference electrodes used in molten salts vary depending on the molten salt itself. The appropriate reference electrodes

in this research were employed based on the concept as they have been commonly used in literature (Crow 1994). The silver wire of 1 mm diameter was chosen as a pseudo-reference electrode in molten hydroxide whereas the nickel rod (5 mm in diameter, ADVENT) was used in molten chloride.

3.5. Electrochemical experiments in molten salts

3.5.1. Cyclic voltammetry

In a three-electrode cell, cyclic voltammetry was employed to examine the electrochemical reactions in molten hydroxide and chloride. This examination was performed using a PGSTAT 30 Autolab potentiostat (Ecochemie) which was controlled by a PC utilising the General Purpose Electrochemical Software (GPES). The electrodes (working, counter and reference) were placed in the cell without the surrounded ceramic tubes. In cyclic voltammetry, the working electrode potential is varied linearly (scanned) with time in a uniform saw-tooth wave as shown in Figure 3.5. During this sweep, the instrument will record the resulting current during the entire cycle of forward and reverse potential scans.

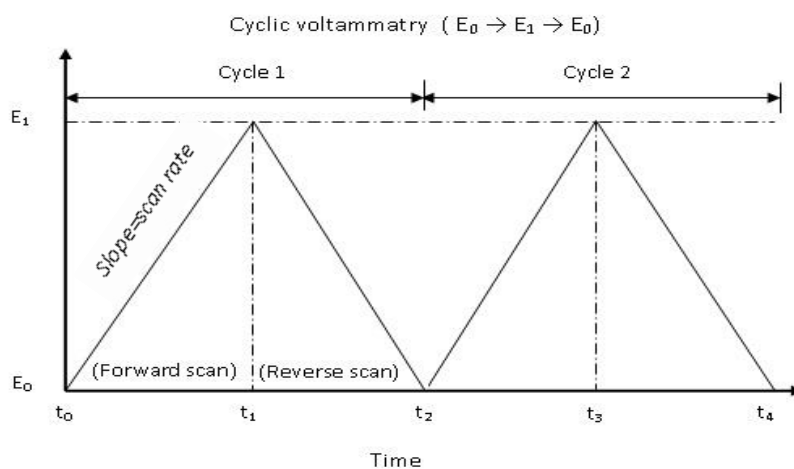


Figure 3.5: Potential time scan in cyclic voltammetry examinations

In all cases of cyclic voltammetry, the potential will change from an initial value (E_0) to a pre-set value (E_1) as shown in Figure 3.5 and then return back to the initial value (E_0). By repeating the potential sweep, multiple cycles can be obtained.

3.5.2. Two-electrode electrolysis

To produce fuel gas from CO_2 and H_2O , electrolysis was carried out in the two-electrode mode employing the Agilent E3633A 20A/10V Auto Ranging DC Power Supply and a laptop with an EXCEL add-in to collect the instrumentation data. Hydrocarbon gas formation can be performed through other chemical reaction mechanisms during the electrolysis and will be explained later. As primary products from the reduction of H_2O and CO_2 , hydrogen and carbon monoxide gases can be produced also at the cathode. For the electrolysis, the applied voltage was chosen as 1.5 V for molten carbonate mixture to avoid carbon deposition which is thermodynamically preferred on the cathode at applied cell voltages above 2 V. For molten hydroxide and chloride, the cell voltage was applied from 2 to 3 V to help search the gases produced in a range that is quite apart from the cathodic limit of alkali metal deposition in molten hydroxide or chlorine gas evolution in the case of molten chloride. Apparently, the electrolysis is designed to study the effect of applied voltage, feed gas composition, temperature and molten salt composition on the production of fuel gases in general and hydrocarbon species particularly.

3.6 Hydrocarbon gas characterisation using different techniques

3.6.1 Gas chromatography

Gas chromatography (GC) was used to analyse the gas products generated from electrolysis. Figure 3.6 shows the schematic diagram of a normal GC. The task of the GC is to vaporise the injected sample and split it between mobile gas phase which is the carrier gas and a liquid or solid stationary phase inside a column. There are two types of column used in the GC, capillary column and packed column. Capillary columns are fabricated from high purity tubing silica (fused silica) with diameter of 0.1-0.5 mm. The tubes are covered by an outside coating of polyimide for strength and protection.(Skoog A. 2000). Packed columns are made from glass or metal tubes of 2-4 mm internal diameter. The packing material is uniformly wetted by the liquid phase and stable at the elevated temperatures (Skoog A. 2000). When the gas sample enters the column, different species will be eluted at different times depending on their boiling points, polarity and thermal/catalytic stability (Skoog A. 2000). A signal can be collected afterwards by the appropriate detector and displayed by the data system. Different types of detectors are used in the instrument such as the Flame Ionization Detector (FID), Thermal Conductivity Detector (TCD), and Electron-Capture Detector (ECD).

The FID detector is mostly used for organic compound analysis whereas the TCD detector is generally used for a wide range of both organic and inorganic species.

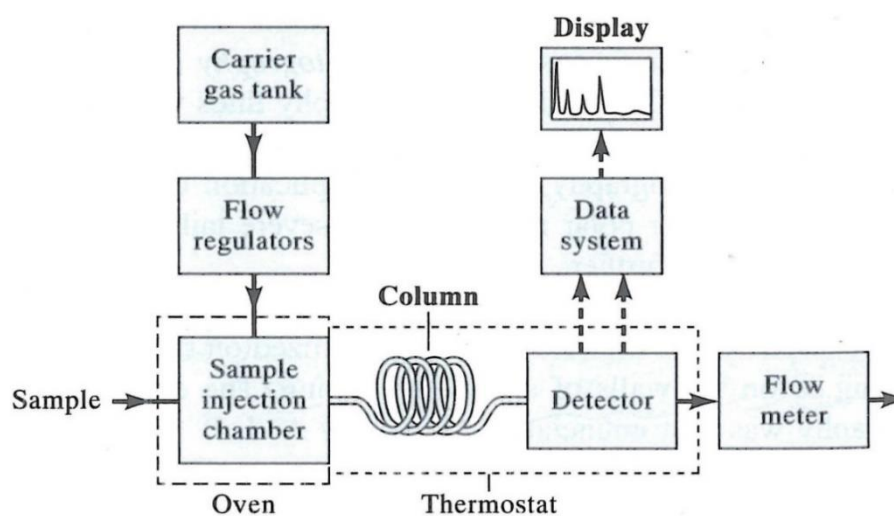


Figure 3.6: Block diagram of gas-chromatographic instrument. (Skoog A. 2000)

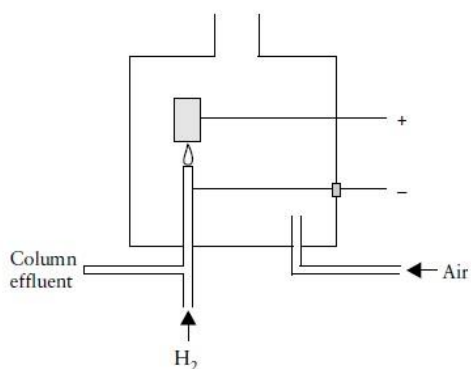


Figure 3.7. Schematic diagram of the Flame ionisation detector (FID) (Higson 2004).

In the FID, a pair of oppositely polarised electrodes is placed near a hydrogen/Air flame as shown in Figure 3.7. After eluting from the capillary column, the carbon containing compounds (hydrocarbon species) are polarised

by the heat of the flame producing cationic intermediates and electrons which act as charge carriers and generate current between the electrodes. The current will be amplified then and recorded as chromatographic peaks.

Whereas in the TCD, the gas eluting from the packed column mentioned previously is passed over a filament wire heated by electricity as shown in Figure 3.8. The resistance of the wire will change depending on the thermal conductivity of the gas. This change will be, in turn, modified by the existence and concentration of the gas analyte in the gas stream sample. The free gas sample (with only a carrier gas (argon)) cools the filament and therefore, even a small amount of an analyte (CO_2 , H_2 etc.) can heat the filament.

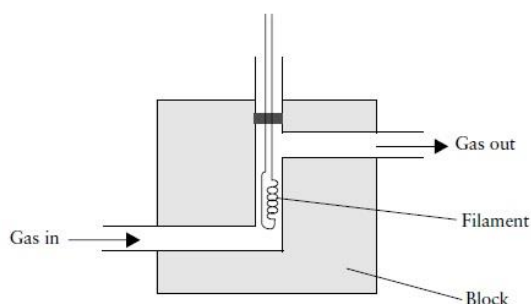


Figure 3.8. Schematic diagram of the Thermal Conductivity Detector (TCD) (Higson 2004).

In this research, the PerkinElmer Clarus 580 type instrument was used for gas chromatographic analysis (GC) of general light hydrocarbons ($<\text{C}_6$). The Clarus GC has an FID channel to analyse the hydrocarbon gases and another channel to analyse the non-hydrocarbon gases using the TCD detector. It is worthwhile to mention that H_2 can only be detected by the Clarus GC. In this instrument, gas separation was performed using an RT® Alumina Bond/KCl capillary

column (30 m x 0.32 mm i.d., 5 µm) with helium as the carrier gas for hydrocarbon analysis and a Haysep N6 packed column (60-80, 7'x1/8" sulfinert) with argon as a carrier gas for non-hydrocarbon analysis. The oven program of 60 °C (hold for 13 min) to 160 °C (hold for 2 min) at 10 °C/min was used for both the TIC and FID channels.

The cathodic gas product from the electrolyser was not flowed directly to the GC to be analysed. An appropriate gas sample to be analysed should be taken by a tedler 1 L (SKC Ltd.) gas bag to the instrument bench as a small amount (5 mL) of gas can be drawn up by a gas-tight syringe. The gas sample is then injected to the chromatograph.

The gas species in the sample were identified and quantified by comparison to two calibration gas standards. The first one is the permanent gas standard with composition of H₂ 10%, CO₂ 10% and CO 40% for TCD detector and the second standard calibration gas contains ethane (C₂H₆) 0.2%, propylene (C₃H₆) 0.2%, 1-butene (C₄H₈) 0.2%, 1-pentene (C₅H₁₀) 0.2%, methane (CH₄) 20%, ethane (C₂H₆) 10%, propane (C₃H₈) 5%, n-butane (C₄H₁₀) 2%, n-pentane (C₅H₁₂) 1% for the FID detector. The remaining composition of both gas standards was balanced with helium gas. Due to limited gas calibration availability for the second standard, another hydrocarbon gas standard containing (CH₄ 20%) was used instead. To check the calibration for the other hydrocarbon species (C₂-C₅ alkanes and alkenes), several samples with different concentrations (from both hydrocarbon standards above and diluted with argon gas) were drawn and analysed to obtain the response factor (F_i) for each substance in each sample (i). The response factor was calculated as follows:

$$F_i = \frac{A_{gas}/M_{gas}}{A_s/M_s} \quad (3.1)$$

Where,

A_{gas} is the area under the peak resulting from the FID analysis for the individual gas (C₂-C₅) in the sample. A_s is the area under the peak resulting from the analysis of the specific gas standard (CH₄). M_{gas} is the concentration (percentage %) of the individual gas in the sample. M_s is the concentration (percentage %) of the specific standard gas in the sample.

The average response factor ($\bar{F}_i$) for each gas species was calculated by equation 3.2 and listed in Table 3.4:

$$\bar{F}_i = \frac{\sum F_i}{n} \quad (3.2)$$

Where, n is the number of samples to be analysed for C₂-C₅ calibration.

Prior to each experiment of analysing the cathodic gas product sample, a small amount (5 mL) from each of hydrocarbon (20% CH₄) and permanent (nonhydrocarbon) gas standards was drawn, injected to the GC and analysed to check the abnormality of calibration and peak shifting (retention time) for each analyte (gas species). The calibration for C₂-C₅ hydrocarbon species will be checked then based on the certainty of peak area and retention time for CH₄ as a hydrocarbon gas standard. Therefore, the instrument would be calibrated every time before the analysis of the intended gas sample by the same day.

Figures 3.10 shows the uncertainties of the recorded detection peak for CH₄ in the hydrocarbon gas standard (only 20% CH₄) and the retention times of elution from the capillary column for 25 samples analysed over 2 years. The retention time of CH₄ seem to be constant with an error percentage of (0-3%) diverting from the corresponding value in the gas standard which is 2.10 minute (Table 3.4)

Table 3.4. Retention times and response factors for the various calibrated hydrocarbon compounds in FID analysis and nonhydrocarbon compounds in TCD analysis.

Gas	Retention time (min)	Response factor (average)
Methane (CH ₄)	2.1	1.00
Ethane (C ₂ H ₆)	2.5	1.94
Ethene (C ₂ H ₄)	3.0	1.88
Propane (C ₃ H ₈)	4.2	2.75
Propene (C ₃ H ₆)	7.8	2.44
n-butane (C ₄ H ₁₀)	12.4	3.31
1-butene (C ₄ H ₈)	18.0	3.16
n-pentane (C ₅ H ₁₂)	21.0	3.32
1-pentene (C ₅ H ₁₀)	23.1	3.25
H ₂	1.1	1.00
CO ₂	2.1	1.00
CO	9.6	1.00

After the analysis of cathodic gas sample, the concentration of each gas compound (M_{gas}) will be calculated as follows:

$$M_{gas} = \frac{A_{gas}/\bar{F}_i}{A_s/M_s} \quad (3.3)$$

The response factor for (H₂, CO₂ and CO) is 1.00 as the GC is calibrated with the permanent gas standard each time.

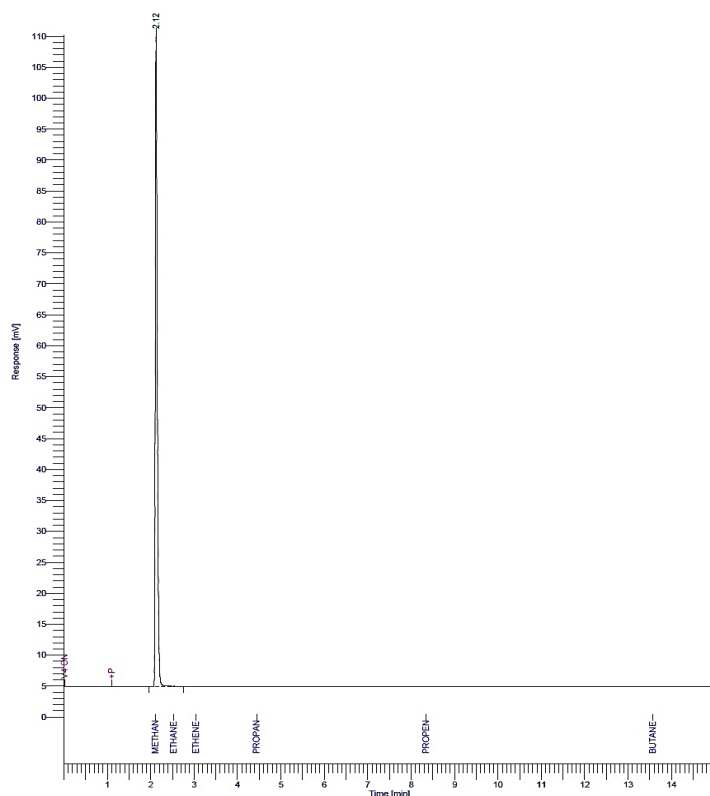


Figure 3.9: FID analysis of one of the calibrated hydrocarbon gas standard containing 20% CH₄.

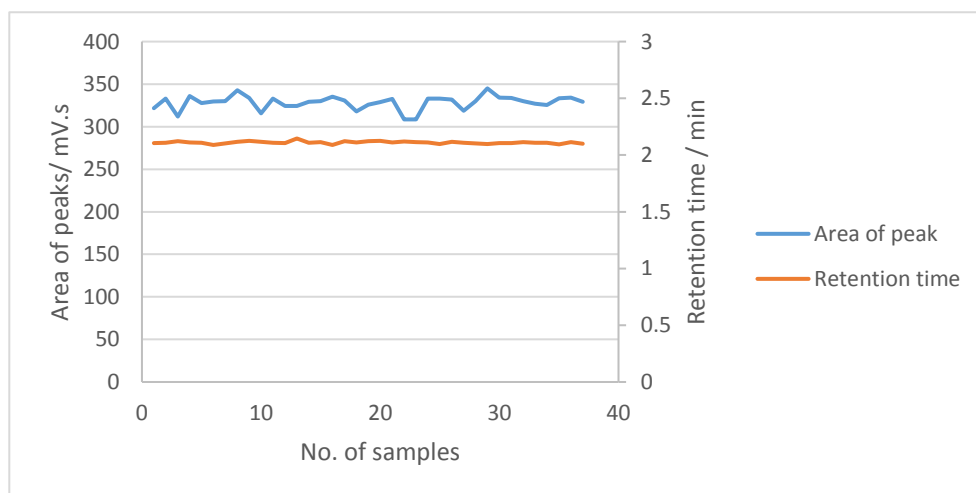


Figure 3.10. Uncertainties of the areas of peak of methane and its retention time rerecorded by the GC using the FID detector.

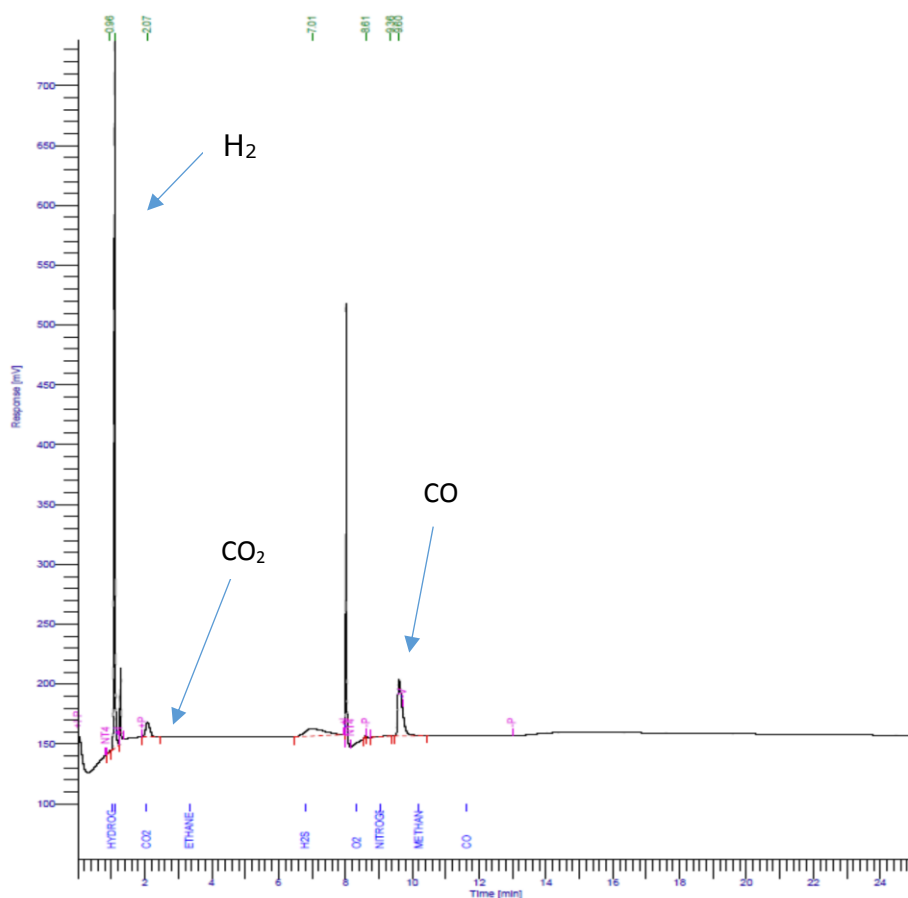


Figure 3.11: TCD analysis of one of the calibrated permanent gas standard containing 10% H_2 , 10% CO_2 and 40% CO .

3.6.2 Gas chromatography-mass spectrometry

Some unknown hydrocarbon molecules were found in the FID channel analysis in the Clarus GC in a retention time after the (C5-) zone and could not be identified by the former GC. Therefore, these species should be analysed by a different sophisticated GC instrument. Gas chromatography-mass spectrometry (GC-MS) technique was employed to analyse the above molecules generated from electrolysis. Figure 3.12 shows the schematic

diagram of a GC-MS instrument where a GC is combined with a mass spectrometer. Generally, the helium gas is used as a carrier gas. The gas sample compounds are separated by the GC part and elute at different times using a capillary column. After the sample gas has exited the GC, the compounds are bombarded in the MS part by high energy electrons which detach an electron from each molecule and result in positively charged molecular ions (M^+):



The ions fragment further into smaller and more stable ions, typical to the particular structural units existing in the parent molecules (Christian, Dasgupta et al. 2014). After that, an analyser works to separate the molecular ions by the mass-to-charge ratio (m/z). The separated ions are detected by an ion detector and plotted as ion intensity versus m/z by a data system.

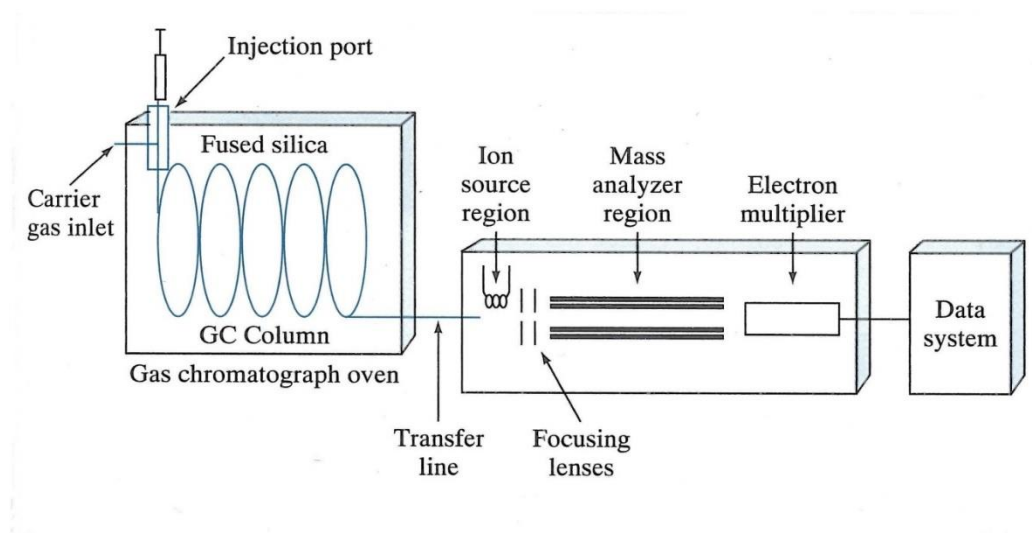


Figure 3.12: Schematic diagram of typically gas chromatograph-mass spectrometer. (Skoog A. 2000)

In this work, the unknown hydrocarbon species were analysed using the Agilent 7890B gas chromatograph interfaced to a JEOL AccuTOF GCX mass spectrometer with an ionising energy of 70 eV and source temperature of 150 °C. The separation was processed on a fused silica capillary column (30m x 0.25 mm i.d. x 25 µm) with helium as a carrier gas. The method of oven temperature programme was employed starting from 40 °C (hold for 2 min) to 350 °C (hold 18 min) at 25 °C/min.

3.7 CO₂ and H₂O analysis by gas detecting tubes.

Gas detecting tubes from GASTEC (ai-cbss Ltd.) were used to analyse the feed gas compositions for CO₂ and H₂O contents. There is an individual detecting tube for each of CO₂ and H₂O as shown in Figure 3.13a,b. GASTEC 2HH and GASTEC 6 types were used to analyse CO₂ and H₂O vapour respectively. The GASTEC tube was broken first from both ends by a particular tip breaker and then inserted inside a pump by the end where the gas direction was marked on the tube itself. The handle of the pump is pulled out for 100 mL sampling. After waiting for the sampling time, the colour of the kit inside the tube will change depending on the gas concentration in the sample. GASTEC 2HH is characterised to detect the higher contents of CO₂ from 5 to 40% of the feed gas, and it contains KOH in the kit so the colour will change from orange to yellow, and the alteration has occurred in result of the following reaction (as the same effect illustrated in chapter 2):



The GASTEC30 tube shown in Figure 3.13b can analyse water content in the range of 0-18 mg/L, and it contains $\text{Mg}(\text{ClO}_4)_2$. However, the colour here will change from yellowish green to purple because of the hydration reaction below:

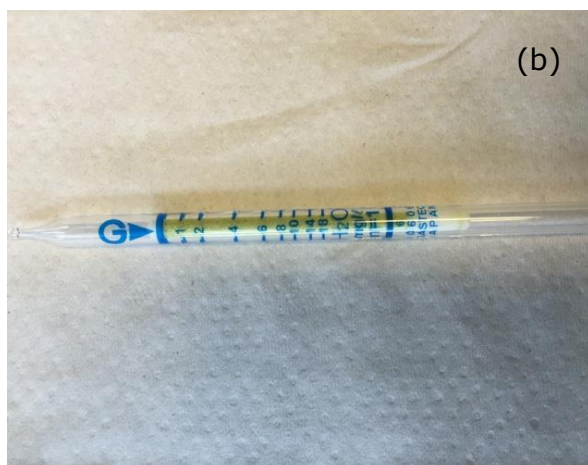


Figure 3.13: Gas detector tubing (a) GASTEC 2HH CO₂ detector tube (b) GASTEC 6 H₂O detector tube.

3.8 Summary

The chemicals, materials and equipments used in this research were listed in the beginning of this chapter. The set-up of the molten salt reactor and the method of operation were then illustrated in details modified from the previous experiments of molten salt electrolysis. Specifications of molten salts used as electrolytes in this project with their justification for CO₂ and H₂O reduction were also outlined. Then, the chapter illustrated the electrochemical experiments of molten salts including cyclic voltammetry and two-electrode electrolysis with detailed specifications of the working, counter and reference electrodes. Finally, the explanation of the analytical techniques used for analysing gas product from electrolysis was provided. These techniques included single gas chromatography and gas chromatography attached with mass spectrometric analysis. The feed gas compositions for CO₂ and H₂O were analysed though using gas detecting tube kits.

Chapter 4

Design and Test of New Molten Salt Electrolyzers for Co-Reduction of Steam and Carbon Dioxide into Hydrocarbons.

The design of an in-house built, new reactor for CO₂ and H₂O co-electrolysis will be explained in detail in this chapter. The illustration of the key parts of this design including electrode selection, feed gas composition and molten salt type, are very important in order to justify the appropriate choices for steam and CO₂ co-reduction. The most crucial function of the new reactor is to absorb large quantities of CO₂ and H₂O in the molten salt.

This chapter is dedicated therefore to the use of a molten salt electrolyser to perform CO₂ and H₂O co-reduction to hydrocarbons. The main objectives are as follows:

- To obtain products of higher calorific values instead of H₂ or CO (carbon monoxide).
- To minimise the amount of CO₂ emitted to the atmosphere from cathode or anode products. This characteristic can be used to capture CO₂ from the flue gas emitted from power stations and industrial fuel gas or oil furnaces.
- To minimise undesired products being deposited on the cathode such as carbon and alkali metals (Na, K, Li) by minimising the applied cell voltage.

4.1. Reactor configuration

Due to the relatively high energy demand of CO_2 and H_2O decomposition (Chapter 2), high temperature electrochemical reduction ($<200\text{ }^\circ\text{C}$) is a suitable way where the rate of the electrode reactions increase rapidly upon heating. High temperature electrolysis can be conducted in solid oxide or molten salt reactors. Many advantages have been found from electrolysis in a molten salt rather than a solid oxide electrolyser, respectively. One of the characteristic features of an electrolyser containing molten salts is that the starting material (CO_2) and products (H_2 , CO , hydrocarbons, O_2) do not mix.

To design a proper molten salt reactor for CO_2 and H_2O conversion, the following aspects need to be considered:

- The cathodic product (H_2 , CO or hydrocarbons) should not decompose or dissolve in the molten salt medium and can be drawn easily out of the reactor as a product effluent. In other words, there is no thermodynamic or feasible reaction with the salt or the electrode material.
- The previous point must be applied for the anodic product (O_2) as well. In the case of O_2 gas, special care must be taken to prevent the salt or electrode undergoing a reaction with the O_2 product (such as molten chloride), particularly at high temperatures ($>700\text{ }^\circ\text{C}$) (Figure 4.4).

Actually, some hydrocarbon species in addition to H_2 and CO fuels were detected in some of the recent investigations using molten carbonates mixed with hydroxides (Wu, Ji et al. 2016; Wu, Liu et al. 2017) (Figure 4.1). However, the method of collecting gases at both the anode and cathode, was not explained in detail.

Some other investigations of molten salt electrolysis have used partitioned cells to separate product gases such as O_2 as the anodic product with CO or other fuel gases as the cathodic product (Kaplan, Wachtel et al. 2010). Figure 4.2 illustrates this cell design, showing that part of the molten salt was in contact with the feed gas of CO_2 . In this process, CO_2 was reduced to CO in molten lithium carbonate (Li_2CO_3) at 900 °C achieving a Faradaic efficiency close to 100%.

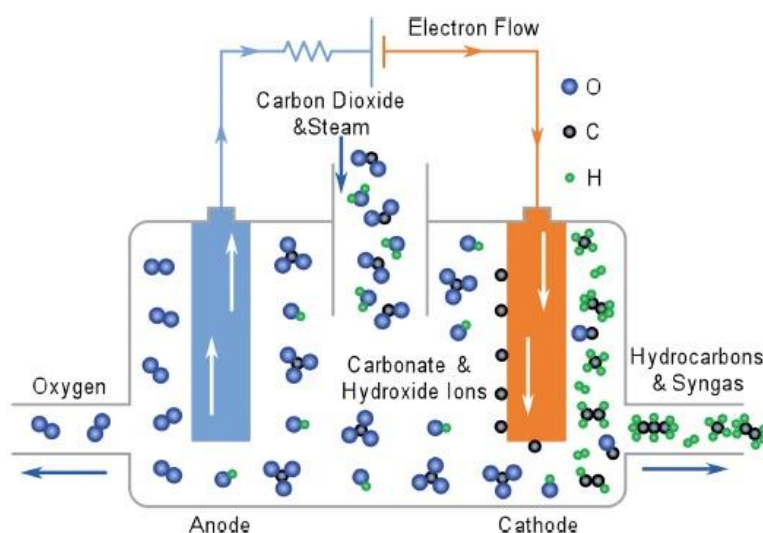


Figure 4.1 Schematic diagram of the simultaneous conversion of CO_2 and H_2O to fuels by electrolysis in a molten carbonate/hydroxide salt (Wu, Ji et al. 2016).

However, open ended tubes were used in other studies to collect and separate product gases or introduce the feed gas inside the molten salt as shown in Figures 4.3 and 4.4 (Laude, Kobayashi et al. 2010; Otake, Kinoshita et al. 2013). These figures are applicable for molten hydroxides and chloride salts,

respectively. Using stainless steel tubes with a dual function for gas pathways and electrode material as shown in Figure 4.4, depends on the molten salt composition in terms of reactivity of the stainless steel with the salt itself. The tubes have been tested and used in a molten chloride mixture to reduce CO_2 to carbon or carbon monoxide (Otake, Kinoshita et al. 2013). In the case of a small scale laboratory crucible as used in this research, it is imperative to use the second design particularly in the event of inserting a cooling water jacket on top for safety issues (Figure 4.3).

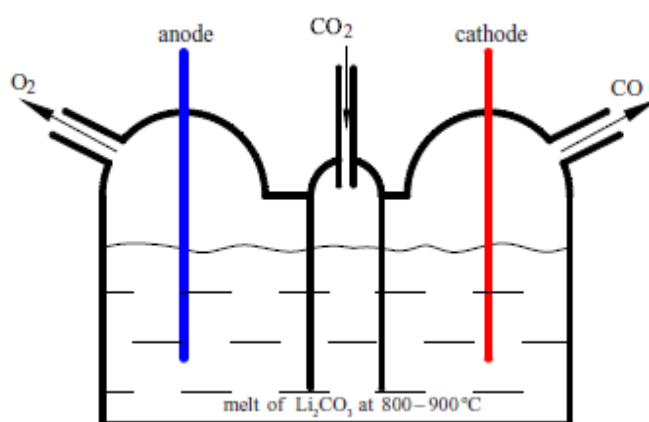


Figure 4.2: Schematic view of the electrolysis cell for CO_2 reduction to CO using a partitioned compartment for each of the cathode and anode gas products (Kaplan, Wachtel et al. 2010).

This particular design however offers less space for CO_2 decomposition inside the tubes in comparison with the initial design in Figure 4.2 because two circular tubes will be inserted in the circular crucible in turn as shown in Figure 4.5 for cathode and anode gas separation, and the subsequent collection. The portion of the salt inside the area bounded by the tube must secure to the largest extent, the unavailability or the scarcity of CO_2 content in the environment from the salt inside the same tube and thus the gas product. The higher the cross-sectional tube area, the lower is the remaining CO_2 content in the product.

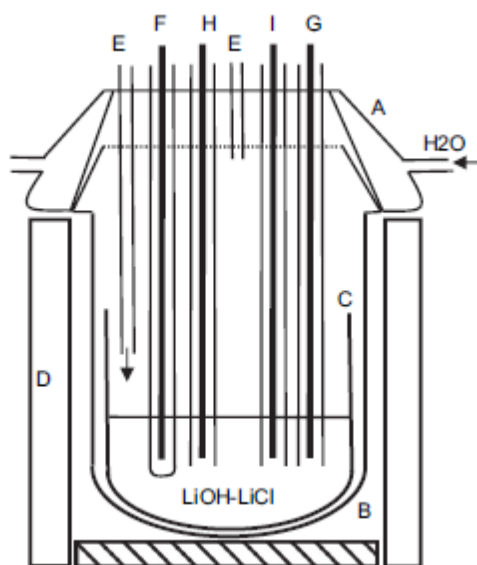


Figure 4.3: An electrolyser with open ended tubes for gas separation and collection. A: cover lid with cooling H_2O , B: reactor, C: alumina crucible, D: electrical furnace, E: argon gas inlet/outlet, F: thermocouple, G: cathode, H: anode, I: reference electrode. Each electrode is sheathed in a tube with both ends open (Laude, Kobayashi et al. 2010).

Nevertheless, ceramic tubes were still used for all molten salt applications in this research and they should be long enough to collect anode and cathode gases from the electrode surface exposed to the molten salt and to guide the gas moving out from the reactor. Moreover, the tubes should be mounted in the lid using silicon stoppers or individual filter adapters as shown in Figure 4.4. The tubes were made from alumina and have adequate resistance to the molten salt attack, resulting in the mitigation of high temperature applications without melting or degradation.

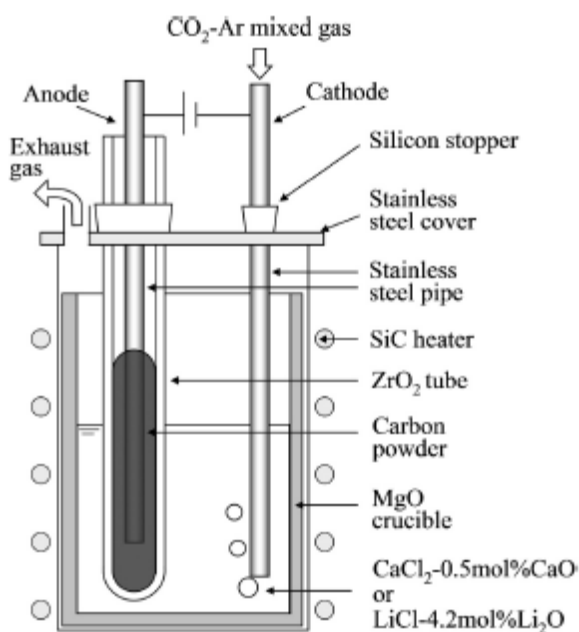


Figure 4.4: An electrolytic cell design for CO₂ direct reduction to carbon or CO using a molten chloride mixed with a minor amount of metal oxides (Otake, Kinoshita et al. 2013).

The most important dimension here is the tube's diameter. Enlarging the tube diameter can contribute to increasing the gas/molten salt contact area, thereby adjusting the cathode and anode gas product composition as the tubes can prevent the electrode from being exposed to the CO_2 environment as illustrated in Figure 4.5. This ends up diminishing the overall CO_2 content in the output.

In the experiment involving the ternary molten carbonate mixture at 500 °C using titanium and stainless steel as the cathode and anode materials respectively for instance, three proper scales of the reactor were tested as given in Table 4.1 (Figure 4.6).

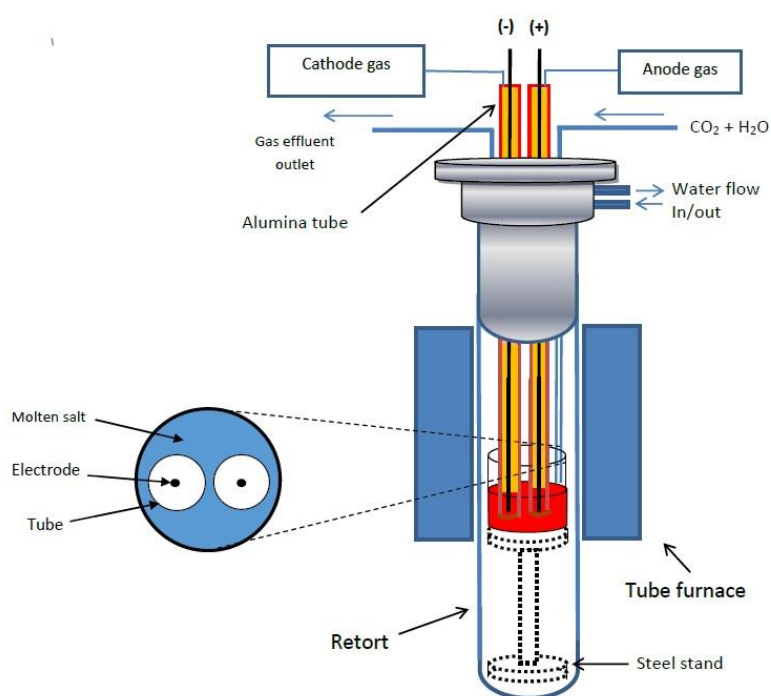


Figure 4.5: The proposed molten salt electrolysis cell configuration in this research enlarging the top cross-sectional view of the crucible to show the area allowing the insertion of two tubes (white circles).

It can be seen in Table 4.1 that changing the reactor scale from 1 to 2 or 3 and then using bigger tubes can give a higher surface area of the melt inside the tube. Consequently, this provides an opportunity for more hydrocarbon gases to be collected from the electrolytic output. A tube with a larger diameter can also help reduce the 'rise' and overall movement of the molten salts inside the tube.

Generally, the amount of salt used should be adequate for CO₂ absorption and decomposition as well as being able to cover an adequate depth of the cathode and anode rods to perform electrolysis, thereby producing various hydrocarbon molecules. Lowering the cathode rod deeper inside the molten salt can contribute to an increase in the total current in the cell for a constant voltage, and a higher energy consumption resulting from electrolysis. If at the same time a higher current efficiency was achieved, a high product yield would also be obtained.

From the point of view of the electrode itself acting as a catalyst, the reduction of CO₂ to the gaseous product is more desirable than to solid carbon for instance, as the latter can cover up the electrode surface, preventing it from catalysing during subsequent reduction. In contrast, the formation of fluid and especially a gas on the electrode, will allow greater surface renewal and hence higher overall catalytic efficiency for the desired product.

Moreover, the partitioned cell configuration offers the opportunity to use the same amount of salt in order to gain a higher depth in comparison with the same crucible without a partition, thus providing the opportunity to use the suitable depth of the electrode in the molten salt as shown in Figure 4.2.

Table 4.1: Specifications of different scales of reactor design, with the average resulting current and hydrocarbon yields for the specified example of ternary molten carbonates at 500 °C.

Specification	Scale 1	Scale 2	Scale 3
Tube inner diameter (mm)	19.5	32	32
Molten salt weight (g)	250	300	500
Crucible inner diameter (mm)	73	85	85
Depth of melt (mm)	25	25	40
Average current (A)	0.015	0.07	0.05
Observed hydrocarbon composition (vol%) in the whole gas product	0	0.15	0.2

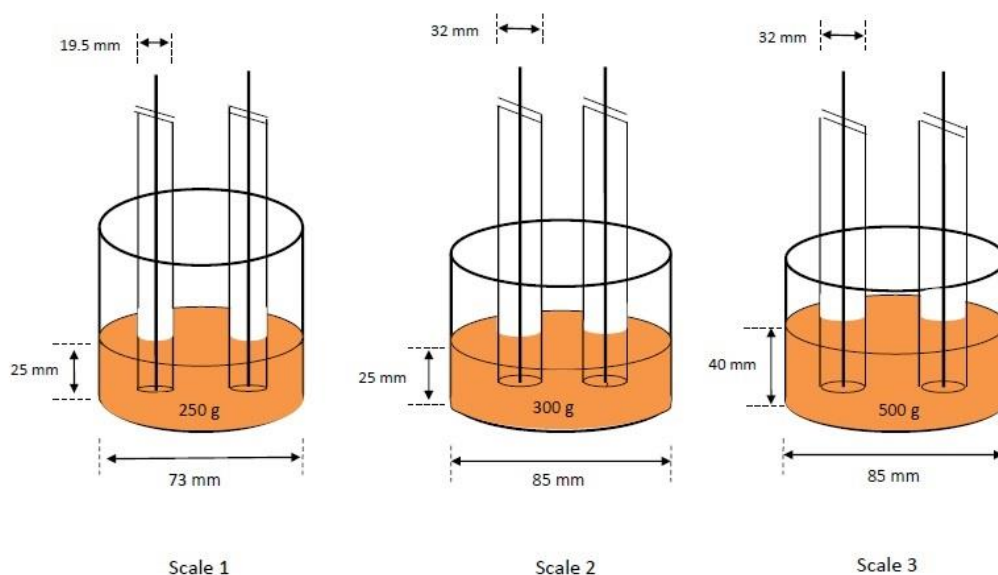


Figure 4.6. A schematic diagram of the different scales used inside the retort (shown in Figure 4.5) and illustrated in Table 4.1.

Therefore, using the crucible design reactor with ceramic tubes like the one illustrated in Figure 4.5, will not provide much more volume or activated surface area inside the ceramic tube than the volume or surface area inside the

partitioned compartment, no matter how large the diameter of the tubes is. As shown in Figure 4.5, the volume of molten salt outside the tubes shown in blue colour is still higher than the summation of two volumes or quantities of salt inside the tubes. This is due to the circular shape of the crucible that holds the molten salt. As mentioned previously, a higher volume of molten salt inside the partitioned compartment or ceramic tube will be very important with regards to minimizing the CO_2 content in the product and thus increasing the hydrocarbon yield.

Yet, it would take a greater effort to fabricate a partitioned cell in this research because the cell is a ceramic crucible. Instead of modifying the crucible, the same partitioning idea was achieved using a larger quantity of salt in the same crucible to insert electrode rods much deeper into the molten salt as shown in Figure 4.7a.

To summarise the comparison with other cell configurations in the literature, the present electrolyser resembles the design illustrated in Figure 4.2 where CO_2 content is minimised in the environment due to the presence of the salt surface inside the tube which ends up increasing the hydrocarbon product yield. Secondly, the ceramic tubes themselves offer a proper way to collect the product gases (produced at the cathode and anode in the salt) out of the reactor as illustrated in Figure 4.3.

It is worthwhile to mention that the reactor was designed to secure the transfer of CH_4 or any produced hydrocarbon molecule from the cathodic or perhaps anodic ceramic tube (by chance) if the gas effluent from the retort outlet had been closed particularly in the case of molten carbonates. Though, the gas product molecules could also diffuse through the molten salt and transfer to the atmosphere within the reactor above the molten salt (Figures 4.5 and 4.6).

Nevertheless, in this research the GC analysis had been performed for the cathodic gas product only.

Furthermore, if required particularly in the case of molten carbonates, lowering cathode and anode rods to the same level in the salt away from the end of the tubes (as shown in Figure 4.7b and applied in scales 2 and 3 of Table 4.1) where the edge of the tube just touches the melt surface, would also mimic the configuration of the partitioned cell reactor.

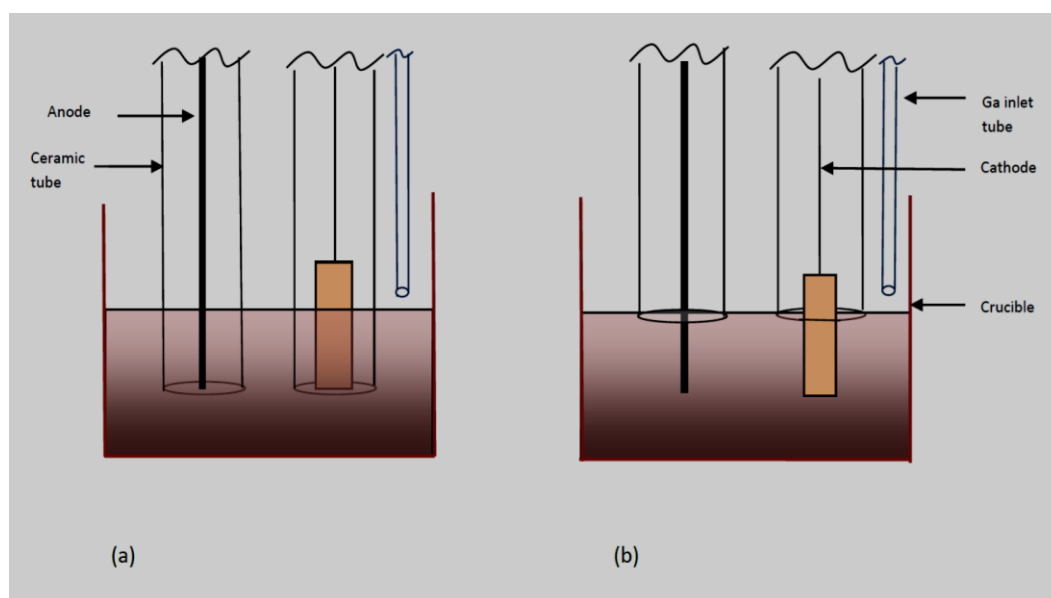


Figure 4.7: The arrangement of ceramic tubes inside the crucible, (a) inside the molten salt surrounding the electrodes (b) lowering the electrodes inside the molten salt without being surrounded by the tubes.

This adjustment will result in better outcomes for hydrocarbon formation than the method of using fully surrounded rods (Figure 4.7a and applied in scale 1) although this setup was expected to collect more product gases from the rod

interface with the molten salt. However, lifting the edge of the ceramic tubes to the melt surface provides a much larger amount of space to submerge the rods in the salt.

Essentially, the manner of using a cathode surrounded by nothing else, was developed from the experiment of molten ternary carbonate electrolysis at 500 °C at applied voltages of over 2 V using CO₂ with 2% H₂O content. In this setup, part of the cathode and anode rods were deliberately brought out from the tube end inside the salt. After electrolysis for 1 hr, the part of the cathode rod outside the tube end was loaded with a much higher amount of deposited carbon than the part surrounded by the tube while both parts were immersed in the molten salt. It seems that the alumina tube wall can impede part of the (O²⁻) ionic pathways inside the salt and thus the passing current and product output were both reduced. However, for the sake of collecting more product gases from the cathode or anode, particularly in the case of molten carbonates, the following steps may be implemented in order to solve the problem if they are applied in scale 2 and 3 only:

1. Closing the gas purging outlet in the reactor lid.
2. Ensuring that no gas is leaking from the silicon bungs to enforce the feed gas passing through the ceramic tubes' gas outlet.
3. Using the minimum possible flowrate of gas feed as required for the entire process.

Then, the gas feed can even flush out the minimal rate of the hydrocarbons produced at the cathode in the molten salt.

4.2. Molten salt type and composition

The most appropriate functions of molten salt fall into the below categories:

1. The ability to use operating temperatures as low as possible without solidification in order to perform the process in a liquid state on one hand and to enable electrolysis and hydrocarbon formation at lower temperatures on the other hand.
2. The salt should be utilised for capturing CO₂ and its co-reduction with H₂O.
3. The salt should provide a wide electrochemical window, particularly a sufficiently negative cathodic limit in terms of the individual reduction of CO₂ and H₂O to CO and H₂ respectively.

In general, most molten salts provide fair capacities for H₂O absorption at different limits (Oblath 1981).

4.2.1 Molten carbonates

The ternary mixture of Li₂CO₃-Na₂CO₃-K₂CO₃ (43.5,31.5,25.0) mol% has been chosen as it provides the lowest melting point of 397 °C amongst all forms of inorganic molten carbonates. Keeping the salt in a liquid state is important as the oxide ion O²⁻, must transfer between the cathode and anode inside the salt to enable electrolysis. The most attractive characteristic of molten carbonate salts in general is their high capacity for capturing CO₂. It has been confirmed that in the absence of O²⁻ ions, CO₂ can be dissolved chemically (rather than physically) into binary or ternary molten carbonates using a slurry bubble column through the following equation (Kanai, Fukunaga et al. 2013; Yin, Mao et al. 2013):



And even the more commonly used:



The equilibrium constant (K) of reaction (4.1) is expressed by:

$$K = a(\text{C}_2\text{O}_5^{2-}) / P_{\text{CO}_2} \quad (4.3)$$

Where $a(\text{C}_2\text{O}_5^{2-})$ is the activity of $\text{C}_2\text{O}_5^{2-}$ ion in the salt. For Equation 4.3, another constant should be added to confirm chemical activity. Then, the total measured constant will be ' $K + k_H$ ' according to Claes, Moyaux et al. (1999) as follows:

$$[\text{CO}_2] + [\text{C}_2\text{O}_5^{2-}] = (K + k_H) \cdot P_{\text{CO}_2} = 9.5 \cdot 10^{-2} \text{ mol.L}^{-1} \quad (4.4)$$

The ratio of the two parameters in the last equation for the concentration of physically and chemically dissolved CO_2 respectively, will depend only on the temperature:

$$[\text{CO}_2] / [\text{C}_2\text{O}_5^{2-}] = k_H / K \quad (4.5)$$

Actually, the physical solubility can be neglected in comparison with chemical solubility (Claes, Moyaux et al. 1999). The gas chemical solubility increases with increasing temperature, reaching as high as 100 mol/m^3 for ternary molten carbonates ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$) at 700°C and atmospheric pressure. The chemical solubility can be elucidated also by the CO_2 liquid phase mass transfer coefficient ($k_L a$) as it decreases with increasing temperature, allowing a larger amount of fresh CO_2 gas to be absorbed according to the following equation (Kanai, Fukunaga et al. 2013):

$$\ln \frac{C^* - C_0}{C^* - C_L} = k_L a t \quad (4.6)$$

Where,

C^* = solubility of CO_2 in the molten salt.

C_0 = the initial concentration of CO_2 .

C_L = the CO_2 gas concentration at any time, t .

The coefficient ($k_L a$) will decrease accordingly with temperature because of smaller surface tension of the molten carbonate at higher temperatures.

In general, this value of solubility of 100 mol/m^3 implies that the salt can absorb or dissolve a volume of CO_2 up to six times the ordinary volume occupied by the salt and this is higher than 100 times the solubility of the gas in the molten chloride. This rise in solubility can also be noticed from the increase of current density during electrolysis as will be shown through the experimental part of this research.

Additionally, it was also assumed that most of the dissolved CO_2 in molten carbonates will be available at the cathode to secure the reduction of carbonate ions to CO or any alternate cathodic product (Claes, Moyaux et al. 1999).

However, it was suggested that the concentration of tetravalent carbon available for reduction in molten carbonates is clearly higher than for gaseous or soluble CO_2 . This can improve the mass transfer kinetics and thermochemical activity as the electrochemical potential will decrease with an increase in reactant concentration (activity) according to the Nernst Equation (Wu, Ji et al. 2016).

Moreover, the presence of H_2O is very important in terms of enhancing hydrogen and hydrocarbon formation. Formation of H_2 gas has been confirmed as a product after adsorption of atomic hydrogen resulting from the indirect

reduction of H_2O in a ternary molten carbonate mixture (White and Twardoch 1984) by the proposed reactions 2.55-57 and 2.52.

However, molten carbonates can sustain higher levels of moisture with the gas containing an adequate concentration of a CO_2 blanket. The hydrolysis due to dissolved H_2O is shown in reaction 2.51 ($\text{H}_2\text{O} + \text{O}^{2-} = 2\text{OH}^-$).

While hydroxide ions are very important in terms of measuring salt corrosion, CO_2 gas can increase salt stability and neutralise the effect of hydroxide ions according to reaction 2.83.

Actually, the presence of hydroxide ion in molten carbonates is not a drawback at all times. Inserting some amount of hydroxide salt (LiOH , NaOH or KOH) into the composition of molten carbonates (such as $\text{Li}_{0.85}\text{Na}_{0.61}\text{K}_{0.54}-2\text{LiOH}$ with a melting point of 335°C) is required for the molar ratio of hydroxides being able to provide adequate H_2 gas for hydrocarbon formation during the electrolysis of the salt itself, without the introduction of CO_2 or H_2O gas at 500°C . The hydrocarbon product can include long-chain species up to $n\text{-C}_5\text{H}_{12}$ with a majority of CH_4 as shown in Figure 4.8.

It is worthwhile mentioning that the long hydrocarbon species in this respect are mainly alkanes (due to the high generation of H_2 from the electrolysis of rich hydroxide mixtures of carbonate salts) compared with the products obtained from the electrolysis of lean hydroxide salts ($\text{Li}_{0.85}\text{Na}_{0.61}\text{K}_{0.54}\text{CO}_3/0.08\text{LiOH}$) illustrated in Chapter 2 that contain some olefins (alkenes) or unsaturated hydrocarbons.

However, due to the competing reaction of H_2 formation (with no H_2O introduction), the depletion rate of superfluous hydroxide salt is faster than the rate of carbonate salt depletion (due to the reduction to carbon or CO) after

120 min of electrolysis, leading to a decrease in H_2 generation and thus overall hydrocarbon formation (Ji, Liu et al. 2017).

Generally, the presence of CH_4 abundantly in the hydrocarbon product can be imputed to the cracking or splitting of long-chain species to shorter molecules at high temperature electrolysis.

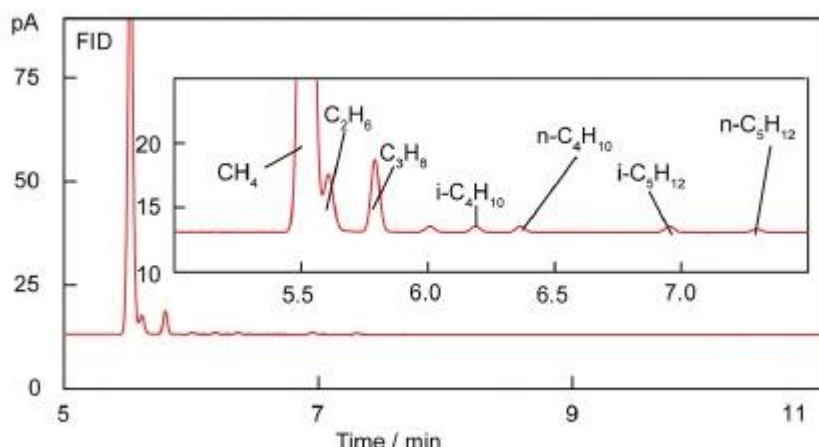


Figure 4.8. GC analysis with FID of the hydrocarbon products obtained during the electrolysis of a high hydroxide mixture of carbonate salt ($Li_{0.85}Na_{0.61}K_{0.54}-2LiOH$) at 500 °C and 2 A constant current with 20 cm² spiral Fe wire as the cathode and 20 cm² spiral Ni wire as the anode (Ji, Liu et al. 2017).

Apart from CO_2 and H_2O electrolysis, molten carbonates have been found to act as an effective heat storage medium for catalysis of reactions at high temperatures with low vapour pressure and high chemical and thermal stability. For instance, the salt that has been used in the molten carbonate fuel cell in which a variety of fuels were used for power production and CO_2 , can be supplied with O_2 as an oxidant. In this cell, the heat of the molten salt medium is used to complete fuel oxidation despite the fact that the Gibbs energy would

not normally support the reaction required to proceed entirely for the generation of electricity.

On the other hand, it was found that molten carbonates can catalyse coal gasification to produce a synthetic gas containing H_2 and CO which can be further transferred into the methane gas in the same medium as the molten carbonate. This process is called Kellogg's coal gasification and follows the reactions as below:



The rate of production of methane depends on the resident time of the two reactions inside the salt.

Also, molten carbonates can promote the partial oxidation of methane to C_2 -hydrocarbons in the case of high melt oxobasicity (low CO_2 gas inlet content). In this case, other active forms of oxide ions such as peroxide (O_2^{2-} , O^-) will be present to perform the reaction (reactions 2.61-63). The process will be explained in more detail later in this chapter.

In conclusion, the electrolyser containing molten carbonate salt has some specific characteristics as summarised as follow:

1. The feed reactants (CO_2 , H_2O) and products (CO , H_2 , hydrocarbons or O_2) cannot be mixed inside the salt but are separated easily by the cathode and anode ceramic tubes to assist with the hydrocarbon generation process and to avoid the reoxidation of the gas product to CO_2 and H_2O .
2. The undesired products of deposited carbon and alkali metal can be avoided by selecting the lowest applied voltages as possible. The minimum amount of

deposited carbon during electrolysis can still be acceptable as the carbon can feasibly react with the produced H_2 to generate CH_4 .

3. The alumina containing material of the ceramic tubes and the crucible can sustain the moderate temperatures ($<700\text{ }^{\circ}\text{C}$) used in this research. Alumina can be dissolved in the melt at higher temperatures and slightly corroded due to O^{2-} accumulation.

4. During electrolysis, the steady state can be reached between the absorbed CO_2 and the reduction of CO_3^{2-} when the current density is stable.

5. The part of the salt inside the cathodic tube should provide the feasibility for the reaction of CO and H_2 (produced previously by electrolysis) through the Fischer-Tropsch process.

6. As CH_4 gas is the most preferred product from the last reaction between 400 and 600 $^{\circ}\text{C}$, feasibility should be ensured also at the same time for the partial oxidation of methane to the various hydrocarbon products as illustrated previously.

Finally, it was clearly suggested that the ternary molten carbonates specified above have been used in this research in regards to the molten carbonate case due to their lower melting point in addition to other motives.

4.2.2. Molten hydroxide

Molten hydroxides have been studied by many researchers for the production of H_2 through the electrolytic decomposition of H_2O , of different types and compositions including lithium, sodium and potassium hydroxides in binary or ternary mixtures. The feasible dissociation of H_2O results from the tenacious absorption of H_2O inside the melt at atmospheric pressure (Divisek 1980). However, electrolysis will be preferred at higher pressure due to the reduced cell voltage but will end up being a more expensive process.

In general, the method of H₂O reduction to H₂ is very attractive and efficient at 350 °C or higher. The operating temperature in molten hydroxides can be generally lower than in molten carbonates (200-400 °C in the case of molten hydroxides), which is favourable for the formation of hydrocarbons in the gaseous state. However, such investigations are still quite scarce. The process was actually omitted from the literature because of the reactivity of CO₂ with molten hydroxides (reaction 2.83) which results in the production of carbonate ions that are listed as non-electroactive ions in a molten hydroxide.

However in another study, CH₄ gas was partially oxidised to C₂ hydrocarbons in molten barium hydroxide as a catalyst at 800 °C (Moneuse, Cassir et al. 1990). The acidity of the melt (O²⁻ concentration) played a significant role in this process. At higher O²⁻ concentrations which results in a more basic salt (reaction 2.71), the melt can catalyse CH₄ oxidation as stated before in a molten carbonate medium (Reactions 2.61-63).

Regarding the reduction of CO₂ to carbon or CO, no detection of such products in molten hydroxides has been reported in the literature, particularly with the rapid reaction of CO₂ in molten hydroxides as stated in reaction 2.83.

However, CO₂ can react with the alkali metal (Li, Na, K) produced at the cathode during electrolysis to form carbon or CO as follows:



The yield of deposited carbon or CO from this process will be assessed based on the current efficiencies obtained during electrolysis. The two products (C, CO) can react further with the generated H₂ (from H₂O reduction) to produce hydrocarbons.

On the other hand, CO_2 can react slightly with the surplus H_2 to form a minor amount of methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) at 220°C using a eutectic LiOH-NaOH mixture (50/50 mole ratio) for instance.

Due to the lower melting point, two molten hydroxide mixtures have been used: LiOH-NaOH with 27:73 mol% and KOH-NaOH with 50:50 mol%.

4.2.3. Molten Chloride

The reduction of CO_2 to elementary carbon was investigated in a molten KCl-NaCl eutectic mixture at 700°C under CO_2 pressure (Halmann and Zuckerman 1987). The formation of deposited carbon or CO was observed with or without mixing with carbonate salts. The mechanism of electrolysis was the same as in molten carbonates (2.36-37). Also, the mechanism of H_2O reduction to H_2 gas on the cathode was the same as for molten carbonates (Kanzaki and Takahashi 1975; White and Twardoch 1987) (reaction 2.68).

Meanwhile, CH_4 gas can be formed by the reaction of carbon or CO with H_2 (reactions 2.53 and 2.5 respectively).

It is preferable to mix molten chloride salts with oxides or carbonate salts to provide O^{2-} ions at an adequate concentration for absorbing more CO_2 gas into the molten salt, thereby increasing the product yield from electrolysis. However, the applied or working temperature of the resulting molten salt mixture will also be high, which is not favourable for hydrocarbon production.

Alternately, a gas feed with a high CO_2 content (90%) at atmospheric pressure can be applied while employing the design of scale no.2 or 3 as a second choice besides the above application.

Essentially due to the relatively high melting point of the above molten chloride salt (KCl-NaCl), the eutectic mixture (KCl-LiCl) with 58.5:41.5 mol% has been chosen instead for molten chloride applications in this research.

4.3. Gas feed composition

Generally, direct production of hydrocarbons from CO₂ and H₂O have rarely been studied in molten salts for either electrochemical or thermochemical conversion.

The composition of CO₂ and H₂O in the feed gas depends generally on the type of molten salt itself. Regarding the H₂O content, it should not exceed 2% of the whole inlet gas (or about 15 mm Hg partial pressure) in any type of molten salt to avoid the high generation of hydrogen gas during electrolysis in addition to the hydrolysis of chloride ions in the molten chloride.

For the molten carbonate case, it has been stated that the mechanism of atomic hydrogen formation (reactions 2.56-57) can only be applicable if the concentration of CO₂ gas is less than 25% of the whole gas inlet. Argon gas can be mixed with the inlet gas to obtain the appropriate gas composition (White and Twardoch 1984).

Methane was the only hydrocarbon produced during some of the molten carbonate electrolysis experiments. The electrolysis produced CO and carbon deposit as well from CO₂ reduction. CO can react further with H₂O at temperatures up to 800 °C to produce more H₂ and CO₂ according to the WGSR (2.11), and the produced H₂ then can react with deposited carbon (at temperatures less than 600 °C) to produce CH₄ (Jaz, Lorenzo 1970).

Regarding hydrocarbon formation, two possible mechanisms can illustrate the process as explained in chapter 2. The first mechanism is the combination of carbon deposited from CO₂ reduction (2.51) with the above adsorbed hydrogen:



Where C_xH_y represents the hydrocarbon formula and can be an alkane, alkene or any other type of hydrocarbon molecule. Reaction 4.11 can be rewritten for methane formation as follows, for instance:



Such produced hydrocarbon fuels can be removed easily from the molten salt using a carrying gas such as argon, CO₂ or H₂O or flushed with the feed gas itself through the ceramic tube.

The second possible mechanism is the partial oxidation of methane produced by reactions 4.12 or 4.8 to C₂-hydrocarbons. Actually, the process was illustrated previously in this chapter and it has been clarified that a low CO₂ content in the gas inlet should be provided. Therefore, in this case, the melt is a more basic and active form of oxide ions such as peroxide (O₂²⁻) or superoxide (O⁻) present in the basic melt and will play a significant role to perform C₂ gas formation according to Frangini (2016)(reactions 2.61-63).

It can be concluded that using a lower CO₂ content in the feed gas (10-25%) in molten carbonates will contribute to higher hydrocarbon formation in terms of higher oxobasicity (reaction 2.63) or from the feasibility of H₂ or H formation (reactions 2.68 and 2.52 respectively).

For the molten chloride case, as the minimum concentration of H₂O should be used, CO₂ gas can be introduced at higher concentrations (>90%) of inlet gas to ensure the high yield of CO or carbon in the product (Otake, Kinoshita et al. 2013).

For molten hydroxide though, CO₂ must be applied with lower concentrations (<10%) of inlet gas to reduce the carbonate ion formation.

In this research, it was found (with regards to H₂O content) that using a CO₂/H₂O ratio between 10 and 15 in the feed gas would result in higher current or energy efficiencies of hydrocarbon gas output as will be illustrated in more detail in the following chapters.

4.4. Electrode materials.

Cathode and anode materials have been chosen based on their resistivity to the molten salt medium and the ability to carry out redox reactions effectively before catalysing the formation of hydrocarbon fuels.

In the case of molten carbonates, the choice of a proper metal for the cathode material is more convenient because the molten salt electrolyte is less aggressive at lower applied temperatures. The temperatures used in CO₂ conversion experiments were significantly lower than 800 °C and can serve dually to reduce metal corrosion while also increasing the hydrocarbon yield.

Due to the effective layer of the metal oxide covering the metal when exposed to molten salts, valve metals (Ti, Zr, Hf, V, Nb, Ta, Al) can be used effectively in a molten carbonate (Baizeng, Xinyu et al. 1998). Actually, the name 'valve metals' comes from the protection layer of the metal oxide.

Iron metal has been used as a cathode material for the particular formation of CH_4 in the co-electrolysis of CO_2 and H_2O in molten carbonates (Wu, Liu et al. 2017). Actually, iron has already been conventionally proven as a catalyst for CH_4 formation (compared to longer-chain hydrocarbons) from the catalytic reaction of CO and H_2 by the Fischer-Tropsch process. Therefore, analogous to this feasible process, a low over-potential can be observed for the electro-formation of methane in particular on an iron metal cathode (Wu, Ji et al. 2016). Nickel has lower activity than iron and a negative effect towards the simultaneous conversion of CO_2 and H_2O , thus leading to an increase in competing H_2 generation (Ji, Liu et al. 2017). Nickel has lower activity than iron and a negative effect towards the simultaneous conversion of CO_2 and H_2O , thus leading to an increase in H_2 generation. As an anode material though, nickel can form a thin oxide layer against corrosion in even hydroxide mixture carbonate salts, particularly Li-containing carbonates.

Titanium (as a valve metal) has been tested to examine strong, controlled oxidation with exposure to molten Li_2CO_3 at $900\text{ }^\circ\text{C}$ in air. It was reported that the TiO_2 layer grew by less than $3\text{ }\mu\text{m}$ in thickness in the first hour. The thickness did not change for the next 100 h (Kaplan, Wachtel et al. 2010).

Therefore, titanium can be a suitable candidate in this work in terms of CO_2 reduction in addition to the availability of its phase diagrams and wide application in molten carbonates.

Titanium was used as the cathode material for the reduction of CO_2 to CO using molten Li_2CO_3 at $900\text{ }^\circ\text{C}$, achieving up to 100% in current efficiency (Kaplan, Wachtel et al. 2010). Besides, it was used also to deposit solid carbon during CO_2 reduction at lower temperatures.

A mild steel rod of 5 mm in diameter was used as a cheaper cathode material for electrolysis in the mixed Li_2CO_3 - Na_2CO_3 - K_2CO_3 with 43.5-30.5-25 mole% at 500 °C, 1.5 V and a $\text{CO}_2/\text{H}_2\text{O}$ ratio of 15.6 in the feed gas. It was observed that the hydrocarbon species in the cathodic gas product ranged qualitatively between C2 and C5 (retention times less than 23 minutes from FID analysis) by 0.03% of the whole gas product in addition to 0.03% of CH_4 . This outcome can support the last mentioned conclusion about CH_4 feasible formation on an iron catalyst. Some other unidentified species over C5 (retention times over 23 min) were found also by 0.06% of the entire gas product (Figure 4.9a).

A titanium foil 1*20*100 mm³ was used as an alternative cathode material for comparison. It was found that the content of C2-C5 species in the gas product in the titanium cathode material case was reduced by 50% to 0.015% while there was an increase in components over C5 by more than 65% over the previous value for mild steel to reach almost 0.1% of the whole gas product (Figure 4.9b). The previous values of hydrocarbon composition in the cathodic gas product are entirely approximate values. Actually, the identification of the corresponding peaks for specific hydrocarbon species (rather than CH_4) in Figure 4.9 (or any chromatogram for the FID channel) is quite difficult by GC analysis solely as the composition of the cathodic gas product is primarily unknown. Nevertheless, the calculation of the gas product contents will be illustrated in detail in the next chapter. It can be concluded at this stage that the products in the case of titanium cathodic material were more specific as found in higher molecular weight, long-chain hydrocarbons and thus offer a higher enthalpy of combustion to produce energy or higher heat values.

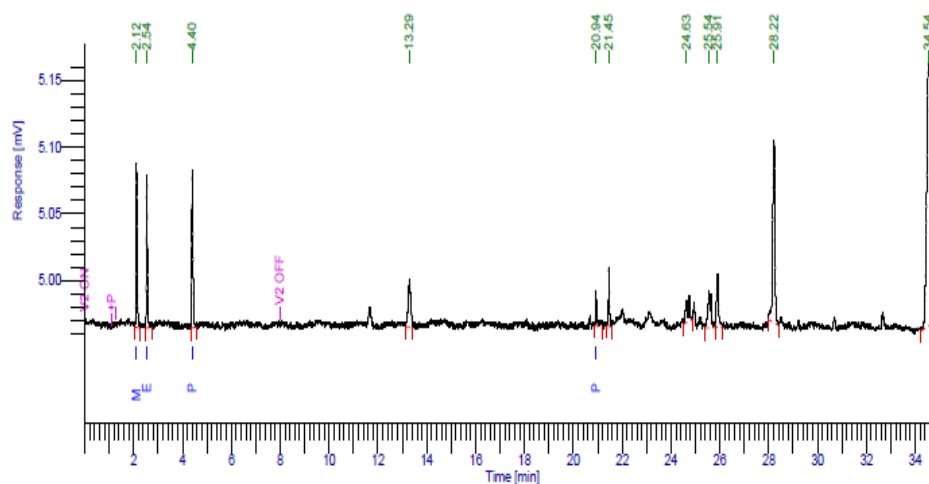


Figure 4.9(a). Gas chromatographic analysis results for cathodic hydrocarbon gases using mild steel as a cathode material.

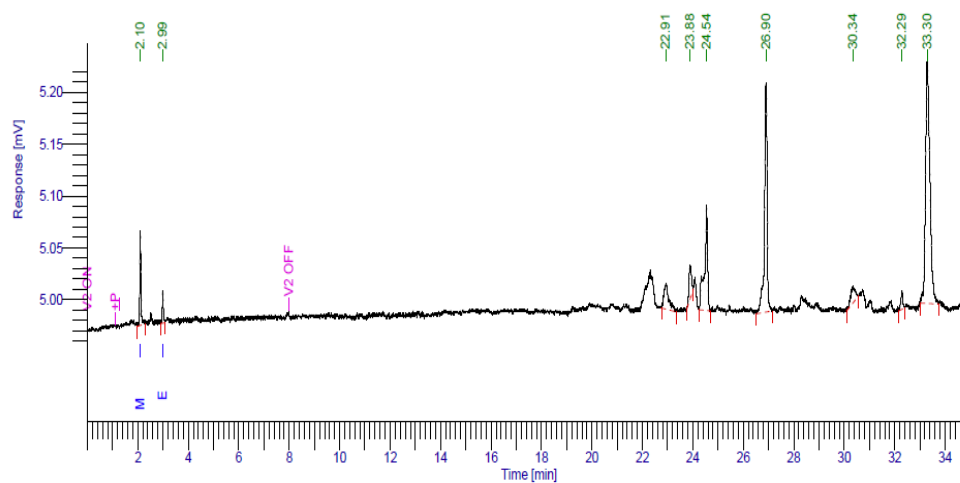


Figure 4.9(b). Gas chromatographic analysis results for cathodic hydrocarbon gases using titanium foil as a cathode material.

4.5. Summary

In this chapter, the new electrolyser for CO₂ and H₂O co-electrolysis was arranged largely based on the configuration of previous investigations. These investigations were dedicated actually to the reduction of CO₂ to CO using a tube or a partitioned compartment to collect the cathodic gases. The parts of the electrolyser are illustrated in detail. Firstly, reactor design configuration was performed in house where ceramic tubes were employed as more convenient partitioned compartments inside the cylindrical crucible to collect cathode and anode gases from molten salts. Secondly, the three types of molten salts including carbonate, hydroxide and chloride types have been examined for the ability of hydrocarbon formulation based on H₂ or CH₄ formation as previously noted in some of the available studies. Thirdly, diluting CO₂ with argon in a humid gas feed introduced into the cell will contribute towards hydrocarbon formation either by the reaction of adsorbed atomic hydrogen with deposited carbon or by the partial oxidation of primarily produced methane.

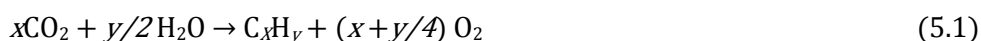
Finally, the electrolyser was tested using two different cathode materials in the ternary molten carbonates (Li₂CO₃-Na₂CO₃-K₂CO₃) at 500 °C with a CO₂/H₂O ratio of 15.6 in the feed gas. It has been found that the hydrocarbon species produced in the case of the titanium foil cathode were specifically higher in molecular weight than the products obtained using a mild steel rod cathode. The production rate of fuels for species larger than C₅ that were produced in the titanium case, was greater than 65% than for the mild steel case. Therefore, the titanium foil cathode material was employed in this research particularly for the molten carbonate case.

Chapter 5

Selection of Molten Salts for Electrolysis of Steam and CO₂

Previous chapters have focused on the sequestration and conversion of CO₂ along with H₂O splitting (or co-reduction of H₂O with CO₂) in molten salt media, where electrolysis is defined as a continuous process despite intermittent shortages in the supply of energy. Therefore, molten salt fluid in general can shift or expand the supplied energy (e.g. heat or electrical energy from solar power plants) depending upon the peak demand for solar energy which has a cyclic variation. Moreover, the calorific values of C-rich products can compensate at least some of the drop-in (input) energy that is consumed during electrolysis. The design of a new in-house electrolyser has been detailed in the previous chapter, with its key aim to perform the co-electrolysis of CO₂ and H₂O using a molten salt solvent as an electrolyte.

Basically, the selection of the molten salt was done based on the ability to generate hydrocarbon fuels from the co-reduction of CO₂ and H₂O. The combination of a hydrocarbon molecule starts ideally from the two known element sources: carbon (C) and hydrogen (H). Both of these elements can be effectively formed from electrochemical conversion via an appropriate molten salt.



Generally, the presence of moisture with CO₂ gas in molten salt experiments is the basis for generating H₂ and CH₄ during electrolysis in most cases (Lorenz

and Janz 1970; Halmann and Zuckerman 1987). Therefore, this chapter is divided into three sections based on the three different types of molten salt mixtures used: carbonate, chloride and hydroxide based respectively.

5.1 Molten carbonate

Previous studies have largely focused on CO₂ reduction to CO or carbon, through the use of different compositions of molten carbonates (Lorenz and Janz 1970; Chery, Albin et al. 2014). Generally, the conversion of CO₂ to CO or C, consumes higher energy during electrolysis and requires the usage of higher temperatures (500-900 °C) to achieve relatively moderate current efficiencies (Kaplan, Wachtel et al. 2010; Yin, Mao et al. 2013). With these severe conditions; Li₂CO₃ (for example) can be dissociated to Li₂O during the reduction of CO₂ to CO at 900 °C using pure Li₂CO₃. On the other hand, it can be noted that the cathodic potential of deposited carbon is 0.4 V (vs. Ag) more positive than the potential of the alkali metal deposition peak observed at the nickel electrode in the ternary molten carbonates (Li₂CO₃-Na₂CO₃-K₂CO₃) at 500 °C. This can be shown in Figure 5.1 (Yin, Mao et al. 2013).

In essence, the possibility of higher hydrocarbon generation can be achieved if CO₂ is mixed with appropriate amounts of water vapour for electrolysis at lower temperatures.

The formation of hydrocarbons can occur indirectly in a molten carbonate through the reaction of CO with H₂ as they are produced primarily from the independent reductions of CO₂ and H₂O respectively (in addition to the prospect of directly forming hydrocarbons through reaction 5.1).

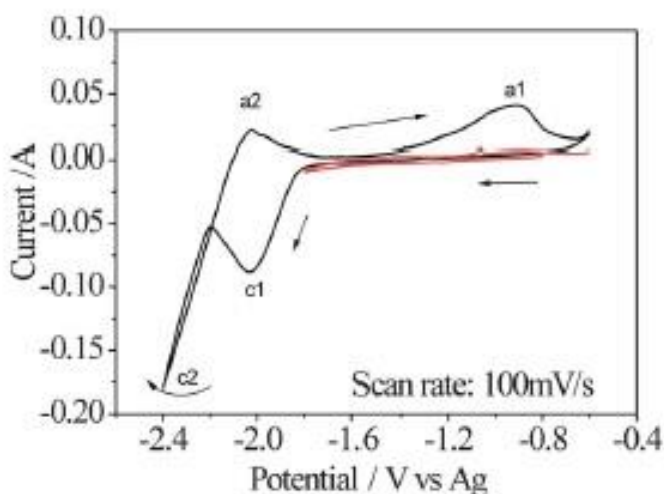


Figure 5.1. Cyclic voltammogram obtained on a nickel electrode with two different potential ranges: (-0.6 to -1.8 V in red) and (-0.6 to -2.4 V in black) in the molten $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ mixture at 500 °C and in a CO_2 atmosphere (Yin, Mao et al. 2013).

The feasible formation of CO and H₂ products associated with carbon deposition has been already confirmed for different molten salts (Chapter 2). As stated before in Chapter 4, the ternary eutectic composition of $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (Molar ratio of 43.5 : 31.5 : 25.0%) was the only molten carbonate mixture that was used in this research due to its relatively low melting point of 394°C. Subsequently, experiments that can be conducted on this salt at a range of 400-450°C for example, can be perfect conditions for efficient hydrocarbon formation.

In the case of electrolysis applied using a titanium foil cathode (dimensions 25*100*1 mm) and a 1.5 V applied cell voltage at 425 °C, the feed gas used was a mixture of CO₂ (48.4%), H₂O (3.2%) and Ar (48.4%). Consequently, the CO₂/H₂O ratio works out to be 15.6. The gas product was forced to flow through the cathode and anode tubes solely through the closure of the gas effluent flow

released from the retort. Titanium metal was used in experiments listed in Chapter 4 as the cathode material for molten carbonates. The feed gas was mixed with an appropriate amount of argon gas to decrease the CO₂/H₂O ratio. It can be seen from Table 5.1 that a significant amount of CH₄, C₂H₄, C₃H₆ and C₄H₈ (as a hydrocarbon gas) were detected using GC analysis with an FID detector. There was some corrections applied to the values of gas composition (vol%) for each product (H₂, CO and hydrocarbon species) due to the fluctuations of the measured peak areas from the FID analysis in the GC. The values of gas product composition with associated volumetric uncertainty are reported in the same Table (5.1) and all the corresponding tables in this research. Also, plots of peak areas in the FID analysis of GC against the volumetric composition for each product are shown in Figures 5.2-5.9 demonstrating the error bars for the drift of the peak area values. All the last plots have relatively got the same slope of nearly 1.0 (or 45° from the x-axis) particularly for the hydrocarbon species as the product composition value was computed based on the peak area of CH₄ gas standard with a response factor of (1.0) (Table 3.4)

Actually, the gas product composition (volume %) was calculated according to Equation 3.3 based on the area of peak shown in the FID detector analysis (M stands for methane, ET for ethane and subsequently ethene, P for propane and subsequently propene, and B for 1-butene in Figure 5.10) and the area of the methane peak in the FID analysis of methane gas standard with the specified gas composition (20%). An average value was taken for two to three different experiments to obtain the gas product compositions for C₂H₄, C₃H₆ and C₄H₈ as shown in Table 5.1.

Table 5.1. Cathodic product gas compositions, current efficiency and the heating value of individual components after electrolysis in molten carbonates at 1.5 V and 425 °C ($A=10.65 \text{ cm}^2$).

Product	Gas product composition (Vol.%)	Uncertainty of gas composition	Production rate ($\mu\text{mol.h}^{-1}.\text{cm}^{-2}$)	Current efficiency (%)	Heating value (J)	Energy consumption (J)
H ₂	0.217	± 0.04	4.4	11.9	11.4	114.2
CH ₄	0.056	± 0.005	1.1	12.5	10.4	
C ₂ H ₄	0.04	± 0.003	0.8	13.2	12	
C ₃ H ₆	0.025	± 0.005	0.5	12.7	11	
C ₄ H ₈	0.026	± 0.002	0.5	17	14.5	
CO	0.58	± 0.09	11.7	31.8	35.3	
CO ₂	52.7	----	----	----	----	
H ₂ O	2.4	----	----	----	----	
Ar	44	----	----	----	----	

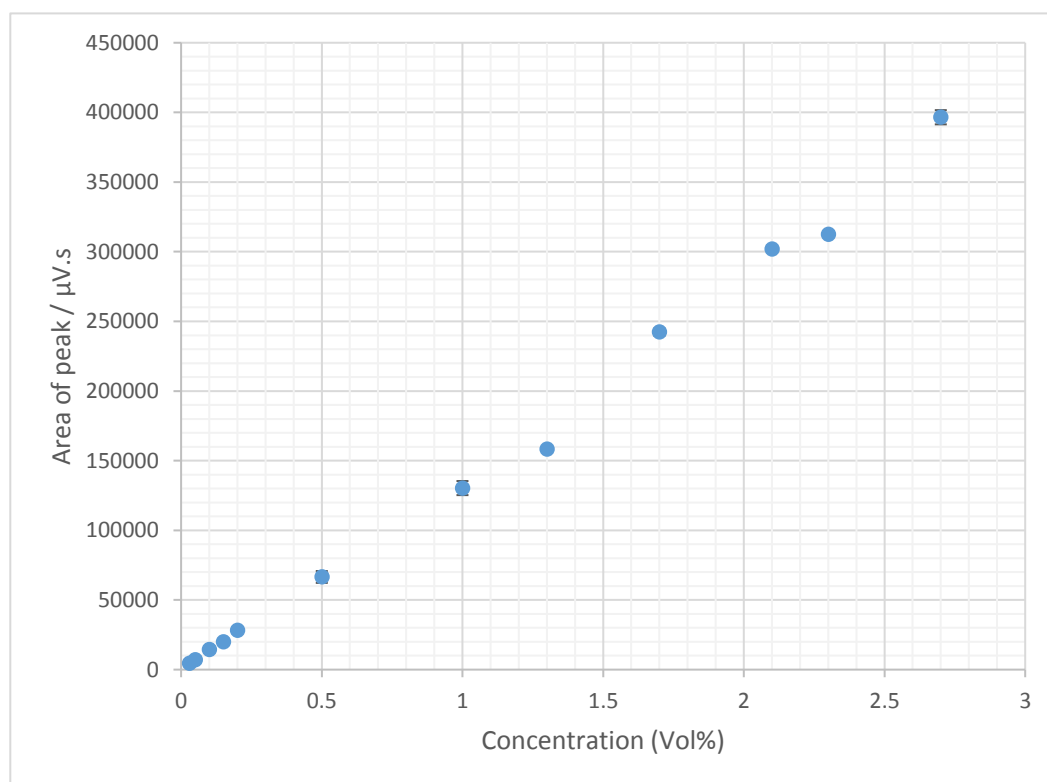


Figure 5.2. Plot of H₂ gas product composition with area of peaks in the TCD analysis. The plot shows the uncertainty of peak area (error bars) at the same gas composition in some points (the gas composition was calculated based on the peak area of H₂ in the standard gas analysis).

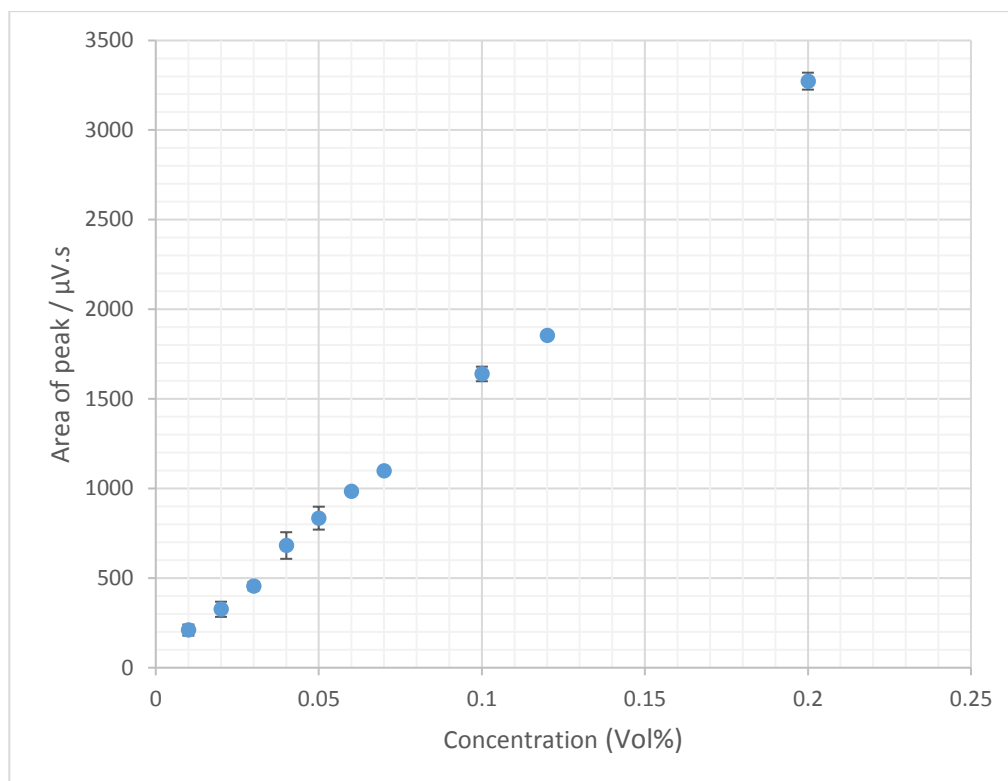


Figure 5.3. Plot of CH₄ gas product composition with area of peaks in the FID analysis. The plot shows the uncertainty of peak area (error bars) at the same gas composition in some points (the gas composition was calculated based on the peak area of CH₄ in the standard gas analysis).

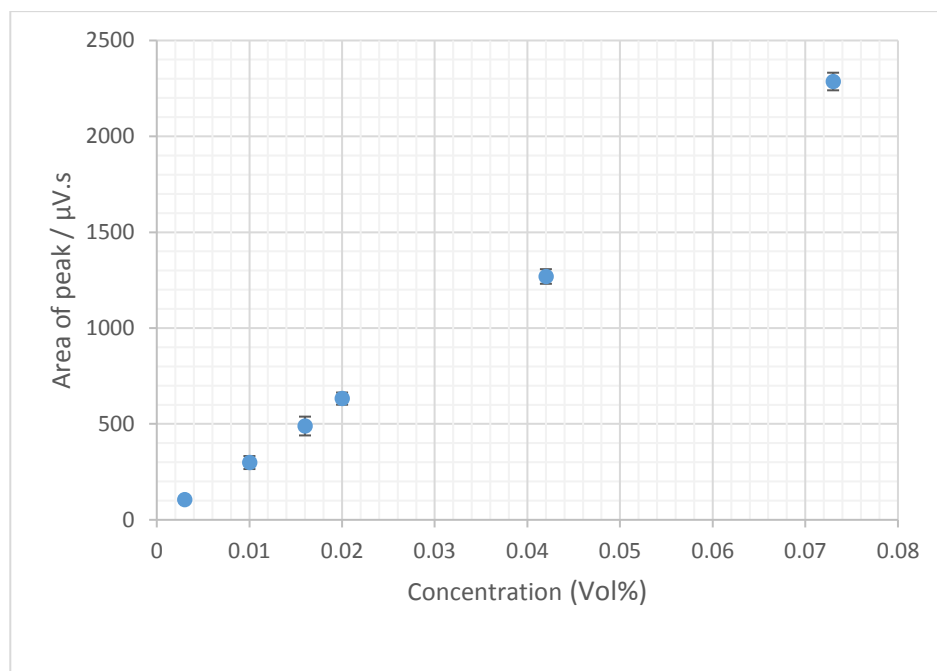


Figure 5.4. Plot of C₂H₄ gas product composition with area of peaks in the FID analysis. The plot shows the uncertainty of peak area (error bars) at the same gas composition in some points (the gas composition was calculated based on the peak area of CH₄ in the standard gas analysis).

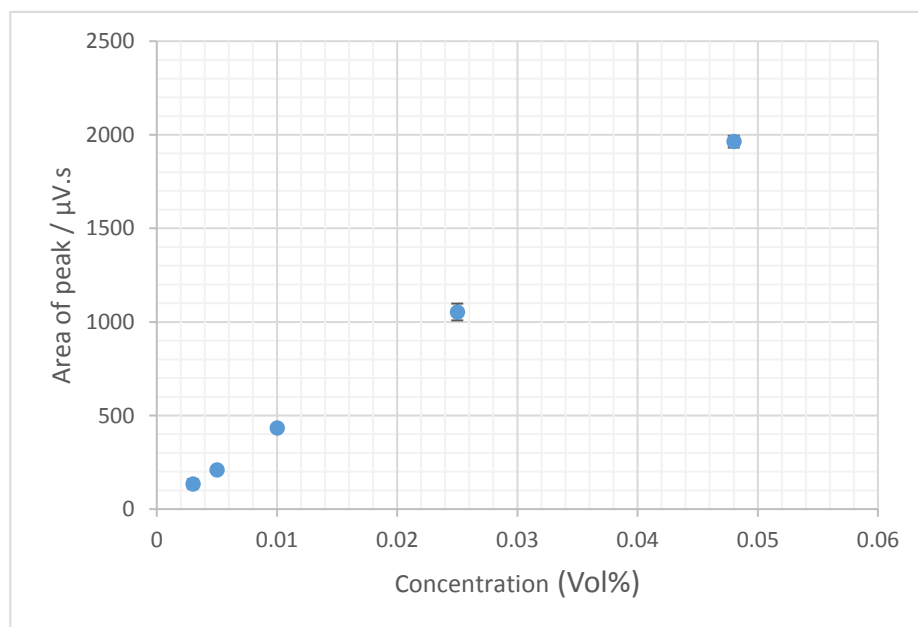


Figure 5.5. Plot of C₃H₆ gas product composition with area of peaks in the FID analysis. The plot shows the uncertainty of peak area (error bars) at the same gas composition in some points (the gas composition was calculated based on the peak area of CH₄ in the standard gas analysis).

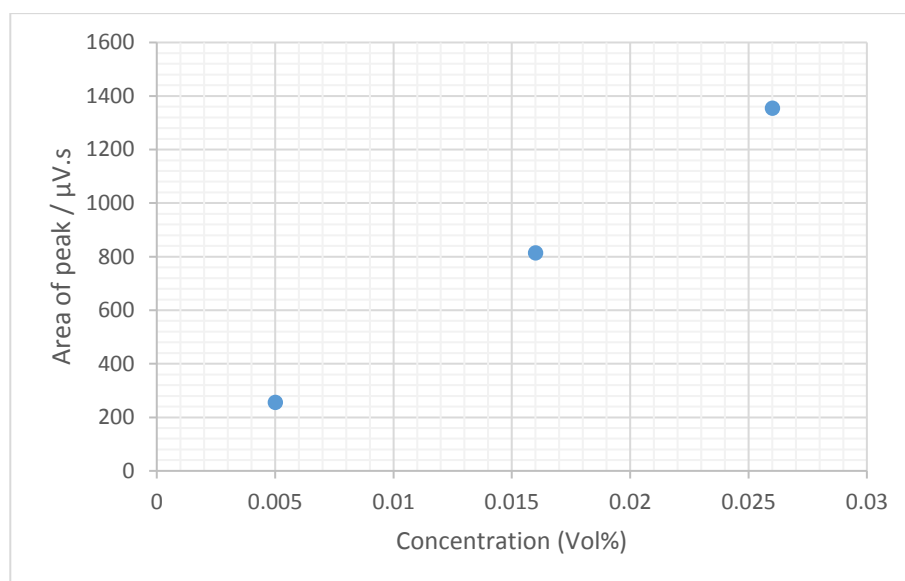


Figure 5.6. Plot of C₄H₈ gas product composition with area of peaks in the FID analysis (the gas composition was calculated based on the peak area of CH₄ in the standard gas analysis).

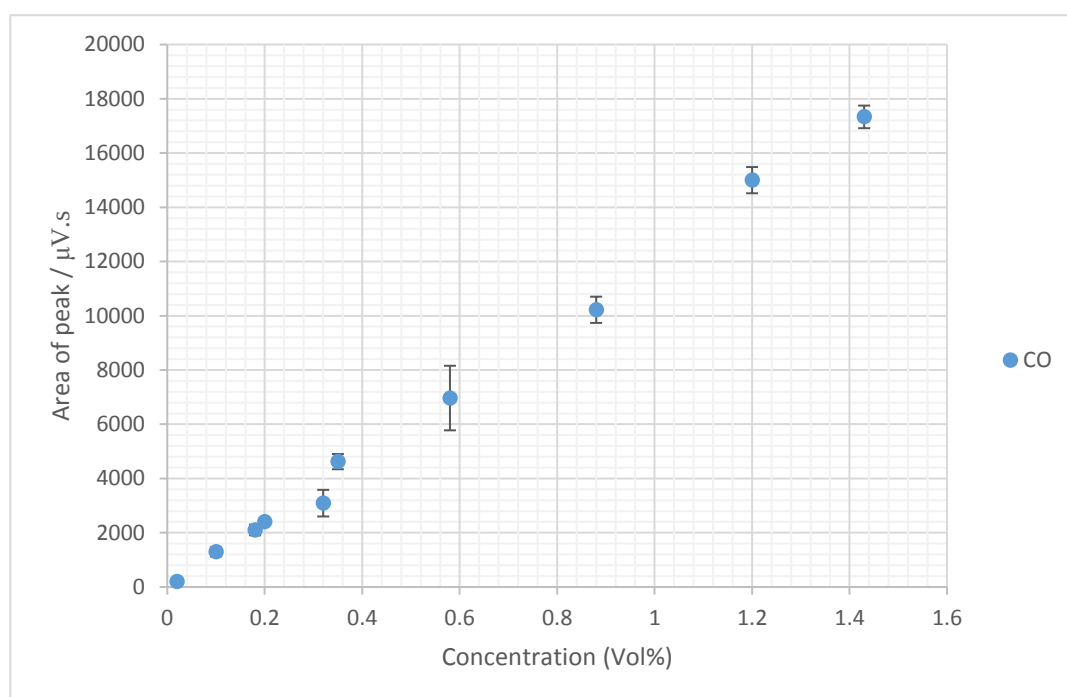


Figure 5.7. Plot of CO gas product composition with area of peaks in the TCD analysis. The plot shows the uncertainty of peak area (error bars) at the same gas composition in some points (the gas composition was calculated based on the peak area of CO in the standard gas analysis).

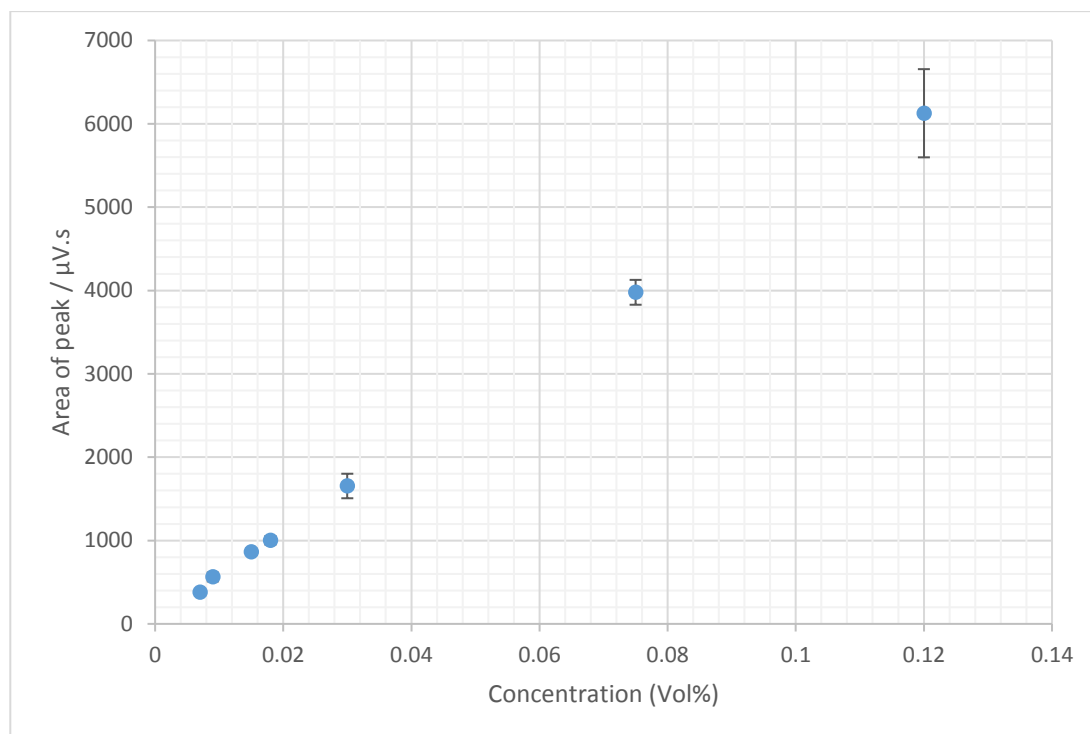


Figure 5.8. Plot of C₆H₁₄ product composition with area of peaks in the FID analysis supported with Mass spectrum analysis. The plot shows the uncertainty of peak area (error bars) at the same gas composition in some points (the gas composition was calculated based on the peak area of CH₄ in the standard gas analysis).

The assignment of the bigger peaks in Figure 5.10 was considered for the previous products (alkenes) with more certainty than the case for the corresponding alkanes (C₂H₆, C₃H₈ and C₄H₁₀) based on the difference in boiling points when eluting from the capillary column to the FID detector in the GC. Also, the certainty of alkene assignment has been made based on the values of gas samples from different cases (temperature, applied voltages and CO₂/H₂O ratio) as will be illustrated separately in Chapter 6.

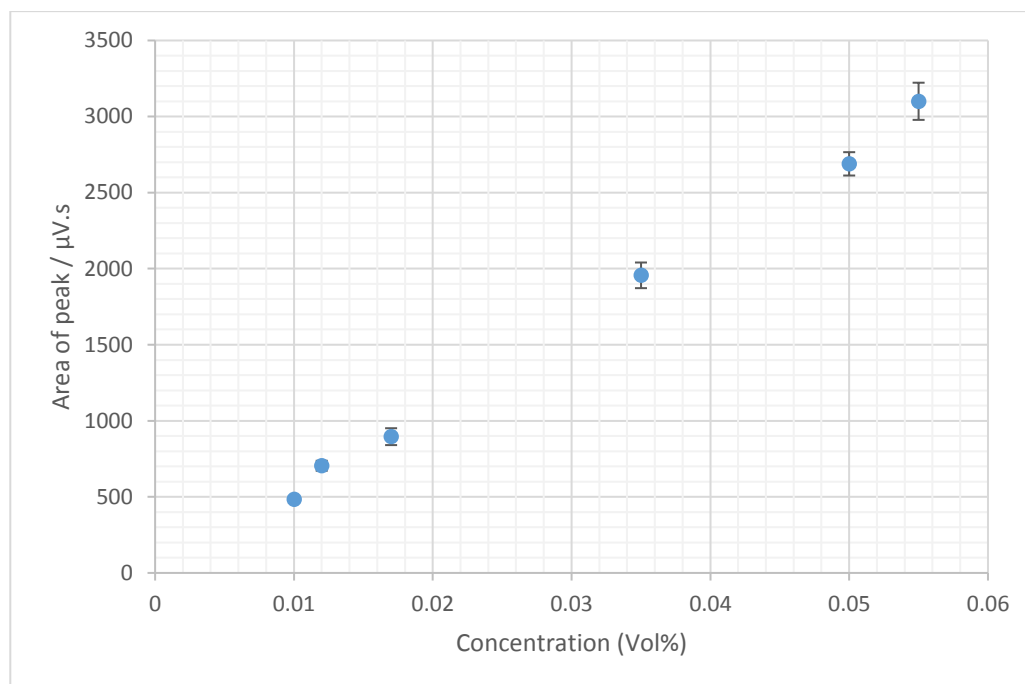


Figure 5.9. Plot of C₇H₁₆ product composition with area of peaks in the FID analysis supported with Mass spectrum analysis. The plot shows the uncertainty of peak area (error bars) at the same gas composition in some points (the gas composition was calculated based on the peak area of CH₄ in the standard gas analysis).

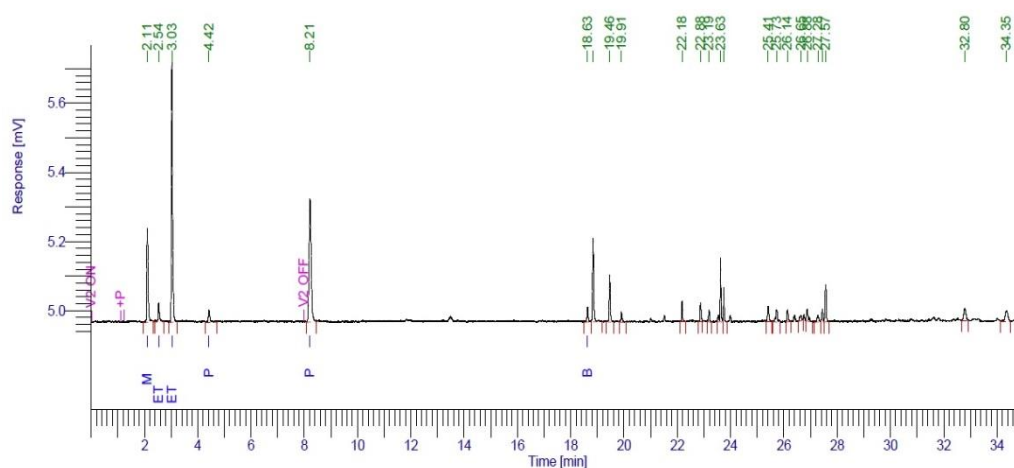


Figure 5.10. GC analysis of the hydrocarbon band for a cathodic gas product after electrolysis was performed in Li₂CO₃-Na₂CO₃-K₂CO₃ (43.5:31.5:25.0%mol) molten salt at 1.5V and 425 °C.

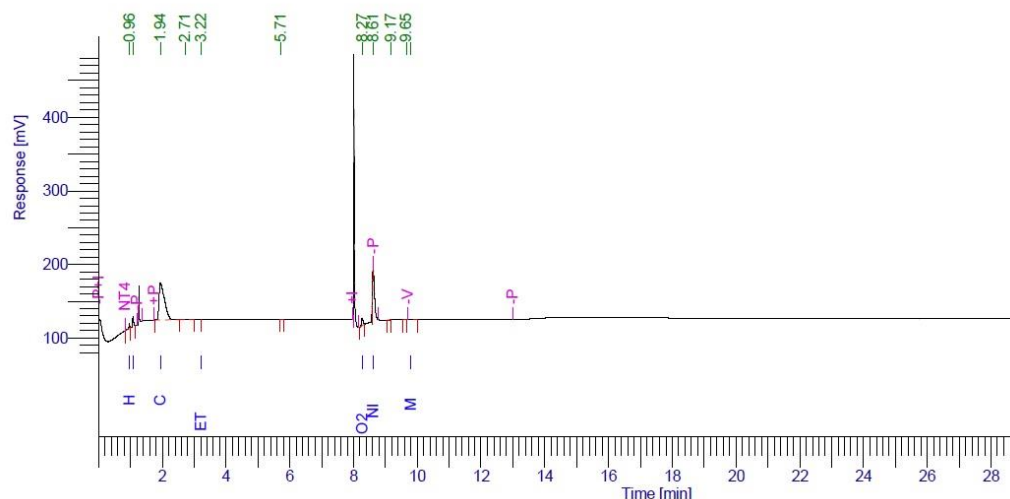


Figure 5.11. GC analysis of the non-hydrocarbon band for a cathodic gas product after electrolysis was performed in $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (43.5:31.5:25.0%mol) molten salt at 1.5V and 425 °C.

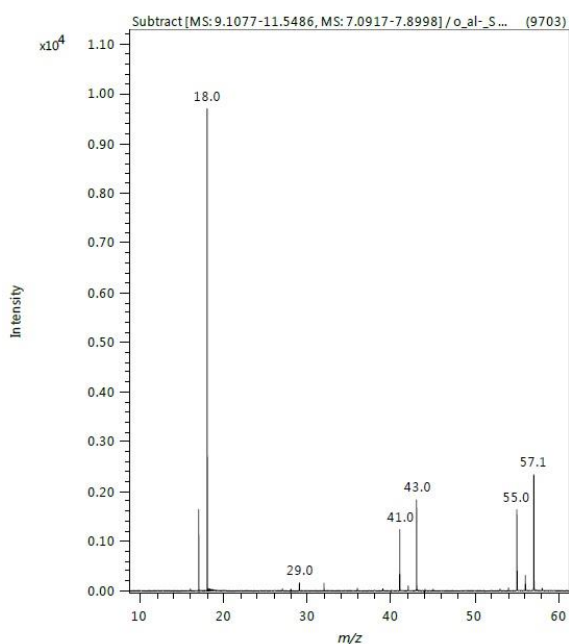


Figure 5.12. Mass spectrum analysis of hydrocarbon gases eluted from the GC column for a cathodic gas product after electrolysis was performed in $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (43.5:31.5:25.0%mol) molten salt at 1.5V and 425 °C. The spectrum was calculated after the subtraction of background gas peaks (permanent gas species shown at all times during the elution from the GC).

The formation of C₂H₆, C₃H₈ and C₄H₁₀ was relatively small compared with the corresponding alkenes. This alkane formation can be confirmed in place of C₂-C₄ alkenes by mass spectrometric analysis (Figure 5.12) as follows:

1. Peaks 57, 43 and 29 stand for the mass of fragments lost from C₄H₁₀ (CH₃CH₂CH₂CH₃), C₃H₈ (CH₃CH₂CH₃) and C₂H₆ (CH₃CH₃) respectively.
2. The last peaks (43 and 29) are produced from the further fragmentation of C₄H₁₀ and C₃H₈.
3. Peaks 55 and 41 stand for the mass of fragments lost from 1-C₄H₈ (for instance) and C₃H₆ respectively.

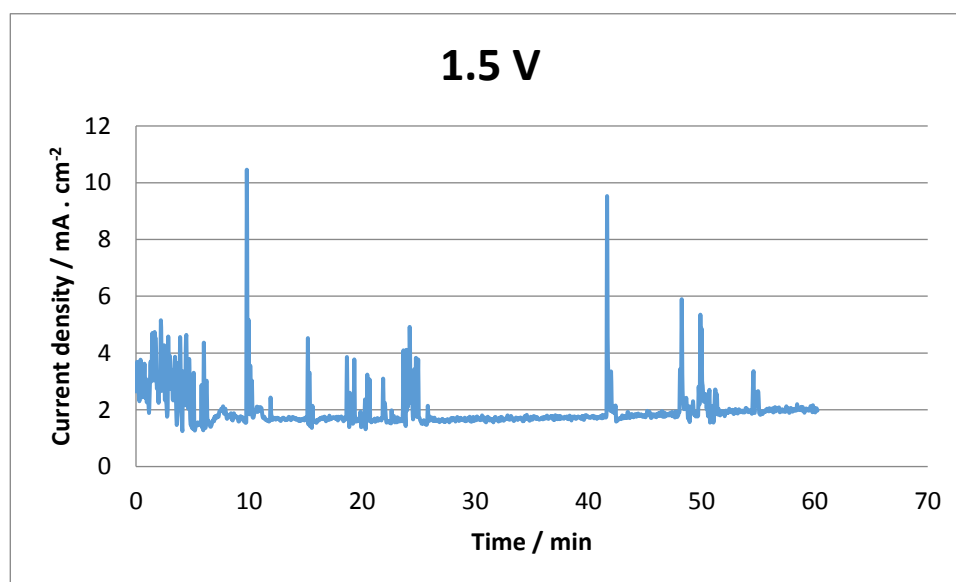


Figure 5.13. Current-time curves resulting from electrolysis performed in molten carbonates at 1.5V and 425 °C.

Obviously, the higher intensity of 57 and 43 peaks in Figure 5.12 does not stand for higher content or concentration of certain compounds (namely C₃H₈ and C₄H₁₀) over certain other compounds (namely C₃H₆ and C₄H₈) when

compared to the intensity of the corresponding species in standard gas with specified alkane and alkene compositions.

On the other hand, some amount of H₂ and CO gases were detected in the product using a TCD detector for the non-hydrocarbon channel in the GC. The volume contents of non-hydrocarbon gases (CO, H₂ and CO₂) were calculated by the same method mentioned above using TCD detector analysis (Figure 5.11). The calculation of current efficiencies will be illustrated later in the next section. The production rates (in $\mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) have been calculated as the number of moles generated for each product per 1 square centimetre of the area of the cathode immersed in the salt, and used during electrolysis for 1 hour of continuous operation. It is worth mentioning that the rest of cathode and anode rods unsubmerged in the molten salt should be covered with alumina (or a suitable material) to calculate the surface area of the immersed rod more accurately.

The number of moles in turn can be obtained from the following formula:

$$N = \frac{\text{Volume of generated gas product (L)}}{\text{Molar volume of the gas } (\frac{\text{L}}{\text{mole}})} \quad (5.1)$$

Where N is the number of moles of generated gas product. The molar volume is defined as the volume occupied by one mole of ideal gas at normal temperature and pressure (NTP) (25 °C and 1 atm). Its value is 24.4 L.mol⁻¹.

It is worth mentioning that H₂ and CO were still the predominant gases during the experiment and the H₂ concentration particularly changed depending upon the H₂O content in the gas feed (or the CO₂/H₂O ratio). Therefore, the higher the H₂O content in the gas feed, the higher the H₂ production rate recorded in the cathodic gas product. The latter was accompanied by a lower hydrocarbon yield rate and this will be explained in detail in the next chapter. Also,

increasing the hydrogen production rate due to the high H₂O content of feed gas would still apply even for molten chlorides and hydroxides respectively. Moreover, the existence of CO as clearly noted from Table 5.1 as a relatively significant amount (in comparison to CH₄), can be imputed to the individual reduction of CO₂ to CO. Actually, CO itself cannot be expected in molten carbonates at temperatures below 775 °C in cases where H₂O is absent (Lorenz and Janz 1970). However, some other authors have claimed that the adsorption and formation of CO molecules can occur on the cathode by CO₂ reduction at low temperatures ($\leq 650^{\circ}\text{C}$), particularly with lower partial pressures of CO₂ less than 1 bar (Chery, Albin et al. 2016). If the reduction of CO₂ to CO is preferred, then H₂ gas will also be formed according to the WGSR (reaction 2.41).

In contrast, CO can be generated by the RWGS (2.42). However, reaction 2.41 is more feasible at temperatures below 817 °C particularly in the event of high partial pressures of H₂O (up to 16.1 mmHg) or 2.1% of gas feed at atmospheric applied pressure (White and Twardoch 1987).

Regarding CO₂ conversion itself, the existence of the gas in the product can be attributed to the following actions:

1. Some of the primarily absorbed CO₂ from the molten carbonates can be flushed from the molten salt surface inside the ceramic tube during electrolysis. This is done due to a draft of feed gas eluted with the cathodic product gas.
2. Some amounts of CO₂ can be produced accompanying the various hydrocarbon species from the reaction of CO with H₂.
3. The difference between the inlet and outlet amounts of CO₂ cannot be ultimately accounted as the transferred CO₂ to CO and hydrocarbon products. Some other amounts of CO₂ can be absorbed chemically in the molten

carbonates. This will basically result in some difficulties in mass balance calculations.

4. The conversion of CO₂ (as is the case with any chemical reaction) cannot be done with 100% conversion in the molten salt, and the unreacted amount of the gas will consequently contaminate the cathodic gas product.

However, in large scale applications, the cathodic product gas with accompanied amounts of CO₂ can be recycled repeatedly with feed gas to increase the ultimate CO₂ conversion rate.

Theoretical justification of hydrocarbon formation

The production of CH₄ can be illustrated in Figure 5.10 and Table 5.1. As clarified in Chapter 2, the formation of this product can be justified due to the reaction of carbon or CO with H₂ as follows:



The Gibbs Energy values were determined at 425 °C (HSC Chemistry software(version 6.12; Outokumpu Research)) as this was the temperature of the experiment. It can be seen from the first mechanism that the production of general hydrocarbons occurs basically from reaction 5.2 with the fresh deposit of carbon and adsorbed atomic hydrogen (H), produced in turn from the individual reduction of CO₂ and H₂O respectively.

On the other hand, the production rates of C₂H₄, C₃H₆ and C₄H₈ (at least) are clearly significant and can approach the rate of methane production itself

(Table 5.1). To justify the formation of these products instead of alkanes or other kind of hydrocarbons, the final mechanisms of hydrocarbon formation listed in Chapter 4 can be reviewed:

1. Reaction of C or CO with Hydrogen.

It can be seen from this mechanism that the production of general hydrocarbons can be performed basically from the reaction of the deposited carbon and adsorbed atomic hydrogen, produced in turn from the individual reduction of CO₂ and H₂O respectively. However, this mechanism does not elucidate about the selective formation of alkenes over alkane as shown in Table (5.1).

The CO produced in excess, can react with H₂ gas instead to produce various species of hydrocarbons through two different routes. The first set of reactions (5.5-5.6) derived actually from reaction 2.5 results in H₂O generation whereas the second set (5.7-5.8) produces CO₂ instead. Since the latter method is more feasible than the method with H₂O formation at higher temperatures as shown in Table 5.2, alkane and alkene products in general are generated primarily through the CO₂ route particularly in media where CO₂ is highly absorbed (molten carbonates). The absorption of some amounts of generated CO₂ can be sustained in the molten salt, particularly inside or near the ceramic tube (as the area is less exposed to the outside CO₂ environment), driving the reaction to the right side and increasing hydrocarbon formation. However, due to the primary production of higher CO rates and in contrast lower H₂ rates, alkene hydrocarbons can be found in a higher proportion than the corresponding alkanes in the final cathodic product.





In reality, reactions 5.5 and 5.6 can be converted to reactions 5.7 and 5.8 respectively by adding the WGSR (reaction 2.41).

The difference between the heat of reaction ($\Delta_r H$) in both cases (where CO₂ and H₂O are formed) of about 38 KJ per gmole per carbon atom of the hydrocarbon molecule, is equivalent to the $\Delta_r H$ of the WGSR (Groggins 1958).

This means that as far as adequate amounts of CO available primarily in the cathodic product goes, the heat of WGSR (exothermic $\Delta_r H$) can be absorbed perfectly by the molten salt. Actually, the liberation of heat (ΔH) for each hydrocarbon molecule in general is still less than the summation of $\Delta_r H$ per mole of CO and H₂ required for the corresponding hydrocarbon.

Moreover, it can be seen from Table 5.2 that slightly less heat (ΔH) is liberated in the formation of alkene in both cases (when CO₂ and H₂O are formed).

Therefore for producing CO₂, the reactions in general will be feasible at 425 °C in contrast with the reactions that lead to H₂O production and become unfeasible from C₂ upwards. Thus the formation of hydrocarbons cannot be sustained above 400 °C.

However from the $\Delta_r G$ data shown in Table 5.2, the formation of larger hydrocarbon molecules (C₂-C₇ or over) can be made possible through the production of CO₂ for alkanes rather than alkenes. This is because as far as

adequate amounts of CO and H₂ are produced from electrolysis, there is sufficient availability for combining on the cathode surface.

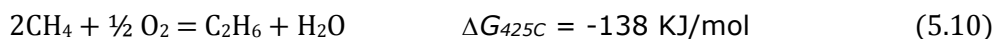
Table 5.2. List of $\Delta_r G$ and $\Delta_r H$ for the generation of some hydrocarbon products from the Fischer-Tropsch reaction (CO₂ or H₂O formed) and partial oxidation of methane at 425 °C. The data were obtained using HSC Chemistry Software (version 6.12; Outokumpu Research).

Product	Fischer-Tropsch Reaction				CH ₄ partial oxidation	
	ΔG (KJ.mol ⁻¹)		ΔH (KJ.mol ⁻¹)		ΔG (KJ.mol ⁻¹)	ΔH (KJ.mol ⁻¹)
	CO ₂ formed	H ₂ O formed	CO ₂ formed	H ₂ O formed		
CH ₄	-61.41	-48.37	-257.7	-220.1	---	---
C ₂ H ₆	-52.03	-25.94	-445.9	-369.9	-138.2	-175.9
C ₂ H ₄	-2.10	23.98	-303.4	-227.4	-297.2	-278.9
C ₃ H ₈	-39.6	-0.47	-549.3	-435.3	-273.3	-267.1
C ₃ H ₆	-5.69	33.44	-423.7	-309.7	-448.3	-387.0
C ₄ H ₁₀	-43.31	8.86	-722.6	-570.6	-424.5	-428.1
C ₄ H ₈	-18.62	33.55	-710.6	-558.7	-608.8	-661.7
C ₅ H ₁₂	-51.10	19.54	-1037.3	-715.2	-579.9	-730.6
C ₅ H ₁₀	-15.78	49.43	-907.8	-717.9	-753.5	-846.7
C ₆ H ₁₄	-40.33	37.92	-1104.4	-876.4	-716.7	-785.5
C ₆ H ₁₂	-14.95	66.35	-1105.1	-744.1	-900.2	-1032
C ₇ H ₁₆	-48.47	42.86	-1272.1	-1006.2	-872.3	-941
C ₇ H ₁₄	-14.11	77.09	-1302.3	-1036.3	-1047	-1216

2. The partial oxidation of methane in molten carbonate

The second proposed mechanism for hydrocarbon formation is the partial oxidation of methane to the various kinds of hydrocarbons as described in Chapter 4. This process can justify the formation of alkenes such as C₂H₄, C₃H₆, C₄H₈, C₅H₁₀ or higher, rather than alkanes in the cathodic gas product during electrolysis. This conditions holds true particularly at a lower CO₂ gas feed

composition level due to the feasible partial oxidation of CH₄ to C₂H₄ (for instance) rather than C₂H₆.



The formation of C₂H₄ or C₂H₆ from methane was successfully conducted even at higher applied temperatures of over 800 °C (Moneuse, 1992). However, the existence of CH₄ will be rare at that temperature due to the subsequent low yield formation from the combination of H₂ and CO.

Basically, the oxidation of CH₄ can be performed in two ways. Firstly, CH₄ gas can react directly with O₂ formed at the anode during the co-electrolysis of CO₂ and H₂O (reactions 5.9-5.10). Some of the produced O₂ can be absorbed inside the molten salt for a short prior to passing through the anode ceramic tube or alternatively, being eluted with the cathodic gas product by the draft of feed gas. Secondly, through the mechanism explained previously in Chapter 4, the absorbed O₂ can be transferred to a more reactive oxide anion like peroxide (diatomic O₂²⁻ or monoatomic O⁻), playing a significant role in the methane oxidation mechanism particularly in the case of low CO₂ concentration levels (reactions 2.61-63).

It can also be seen from Table 5.2 that the formation of higher molecular weight hydrocarbons (larger than C₂) will be more feasible (resulting in a more negative Δ_rG) by this mechanism with the priority on alkenes rather than alkane hydrocarbons.

5.1.1 Current efficiency and energy consumption

The current efficiencies of hydrocarbon species obtained in the molten carbonate case (Table 5.1) are significantly higher than the values resulting from molten hydroxides or chlorides due to the feasible way of hydrocarbon formation, in addition to the higher applied temperatures. Generally, the increase in current with time during electrolysis particularly at high applied voltages, results from the expansion of the cathode surface due to carbon deposition (Ijje 2015). It can be seen from Figure 5.13 that the average current density recorded during electrolysis is around 2-4 mA/cm². The surface area of the titanium plate cathode immersed in the salt was calculated as 10.6 cm². To obtain high total current efficiency, the generation of hydrocarbon species is more desirable than the generation of CO and H₂. The current efficiencies of individual hydrocarbon products would be much higher than H₂ and CO if they were all produced in the same amount. In this case, the charge required for the hydrocarbon molecule is higher than for each of the H₂ and CO products. Basically, for one mole of methane gas for instance, 8 electrons need to transfer inside the salt to produce a molecule of CH₄ (4 for each C and 1 for each H). Therefore, it can be seen from Table 5.1 that the current efficiency of CH₄ is nearly 40% of the CO value although the production rate of CH₄ is just 10% of the CO production rate. The current efficiency can be calculated basically from the following equations:

$$\text{Current efficiency} = \frac{Q_x}{Q_T} * 100 \quad (5.11)$$

$$Q_x = nNF \quad (5.12)$$

Where Q_x is the charge required for the amount of individual product produced; n is the number of electrons required, F is the charge of one electron which

equals 96485 col and Q_T is the total charge calculated from the area under the current vs time curve.

On the other hand, if the applied voltage exceeds 2 V, the formation of the deposited carbon will be rapid and there is not enough time for the hydrocarbon molecule to be produced from the H, H₂, C or CO available during electrolysis. The current efficiency can be higher on this occasion as will be illustrated in the next chapter.

In the experiment carried out previously using molten carbonates and a specific gas feed combination (48.4% CO₂ + 3.2% H₂O + 48.4% Ar) at 425 °C and 1.5 V, it can be seen that the summation of individual current efficiencies for H₂, CO and hydrocarbons can reach 100% (Table 5.1). The higher total efficiency results in significantly lower energy consumption of 114 J for the total fuel produced or just 0.157 kWh per mole of fuel. This value is apparently less than the energy consumed for an optimum deposit carbon operation of 0.456 kWh per mole of carbon (Yin, Mao et al. 2013). However, the determination of energy consumption did not take into account the other energy requirements that can be significant (heating the molten salt itself for instance) as this energy can be provided by the renewable sources (such as solar energy).

In reality, the energy consumption has been calculated from the following equation:

$$\text{Energy consumption} = Q_T * V \quad (5.13)$$

Where V is the applied voltage equal to 1.5 V.

It can be seen from Figure 5.13 that the recorded current resulting from electrolysis above was relatively low as compared to the current resulting from carbon or alkali metal deposition for instance (Ijije, Sun et al. 2014). This can

be imputed to the adsorption of CO and atomic H on the cathode, incurring relatively little current usage during the individual electrolysis of CO₂ and H₂O as illustrated previously in Chapter 2.

It should be noted that atomic hydrogen (H) cannot be directly obtained from H₂O reduction. A bicarbonate ion (HCO₃²⁻) would have to be generated first as an intermediate product prior to its reduction in turn to H. Two atomic hydrogen species can combine in that case to form hydrogen gas (H₂). This gas generation is still largely affected by the presence of H₂O in the molten carbonates, but not as significantly in the case of molten chlorides and hydroxides respectively.

Nevertheless, the resulting current was found to be as low as 0 mA/cm² during electrolysis in the case when gas passage through the cathodic or anodic tube was blocked due to certain reasons (for instance). This action can definitely affect the gas product (CO or H) adsorption step prior to the final generation of hydrocarbons.

On the other hand, the heating values recorded in Table 5.1 were computed as follows:

$$\text{Heating value} = \Delta H_c * N \quad (5.14)$$

Where ΔH_c is the enthalpy change of combustion (absolute) per one mole of fuel (kJ.mol⁻¹). This term is basically the total energy (heat) released when one mole of fuel undergoes complete combustion with oxygen. Table 5.3 below lists the values of enthalpy change of combustion for some common fuels including H₂ and CO.

It can be seen therefore that the energy consumed for hydrocarbon formation can be absolutely substituted by the calorific value (heating value) of fuel (as

it is a hydrocarbon-containing product) when employed (burned or consumed) for energy purposes in factory applications. Moreover, there is no energy penalty at this stage. Hence the greater the product of hydrocarbons obtained, the greater the current efficiency and subsequent energy profit attained. It is very interesting to note that for instance the energy obtained from the summation of heating (calorific) values of cathodic gases produced in the above experiment, was more than 82% of the total consumed energy itself (Table 5.1).

Table 5.3. Molar heat of combustion for some common fuels at 22 °C (Groggins 1958).

Fuel	Molecular weight	ΔH_c (KJ. mol ⁻¹)
H ₂	2	-244
CO	28	-283.24
CH ₄	16	-885
C ₂ H ₄	28	-1411.2
C ₃ H ₆	42	-2057.8
1-C ₄ H ₈	56	-2716.8
C ₆ H ₁₄	86	-4163
1-C ₇ H ₁₄	98	-4658
C ₇ H ₁₆	100	-4817

5.2 Molten Chloride

The attractive characteristic in the molten chloride case is the probability of producing CO or C directly from CO₂ reduction in the presence or absence of a carbonate ion (Halmann and Zuckerman 1987). Carbonate ions are used as an important additive to molten chlorides to provide the oxide ions required for performing CO₂ reduction (Song, Xu et al. 2012) (reaction 2.59).

As stated in Chapter 2, in the absence of H₂O and carbonate ions, the reduction of CO₂ to carbon or CO can be done in several steps (Halmann and Zuckerman 1987):

First step: the reduction of CO₂ to a CO₂²⁻ radical.



Second step: chemical formation of CO.



Third step: electro-reduction of CO to carbon.



In the presence of steam beside CO₂ in the feed gas, the reduction of CO₂ can be more feasible as CO₂ can react with hydroxide ions released, in turn accompanying the atomic hydrogen from the primary reduction of H₂O through to the one-electron transfer reaction:



Moreover, carbonate ions can be generated even from molten chloride through the reaction of CO₂ with oxide ions (reaction 2.59) emitted in turn after the direct reduction of H₂O to H₂ gas;



In addition to the above function of molten chloride, it is possible to conduct the co-electrolysis of CO₂ and H₂O at temperatures even lower than the 400 °C

employed in molten carbonates through a feasible way for hydrocarbon production. However, there is still a lack of evidence in the literature confirming whether carbon or CO can react directly or indirectly with H₂ (or even H) for the sake of hydrocarbon formation if it has been found primarily in the electrolysis product.

To find the effect of CO₂ on electrolysis in molten chlorides, the following experiments were performed:

1. Cell conduction through the design of scale no. 1 as described in Chapter 4 was performed. The feed gas in this instance containing H₂O, CO₂ and Ar at 3.1, 19.4 and 77.5 mole% respectively, was kept flowing over the KCl-LiCl molten salt (41-59 mol%) at 1.3 bar. Two-electrode electrolysis was performed using a graphite rod (10mm diameter) and a stainless steel rod (5mm diameter) as the cathode and anode respectively. Obviously, the feed gas pressure was applied slightly over 1 atm to increase CO₂ activity and thus the opportunity of improving reduction inside the molten chloride. Another experiment was performed at the above conditions using a feed gas containing 3.1% H₂O and with no CO₂. Carrying out electrolysis at 2 V and 375 °C, it can be seen from Figure 5.14 that there is a small difference between the two current curves resulting from electrolysis in both cases. However, the current was still relatively high in both cases and gradually decreased with time. The decline in current can be imputed generally to the drop of oxidant concentration (H₂O, CO₂) that is reduced on the cathode surface due to the accumulation of new products (such as H or H₂ bubbles) as there is no renewal action on the cathode surface during electrolysis.

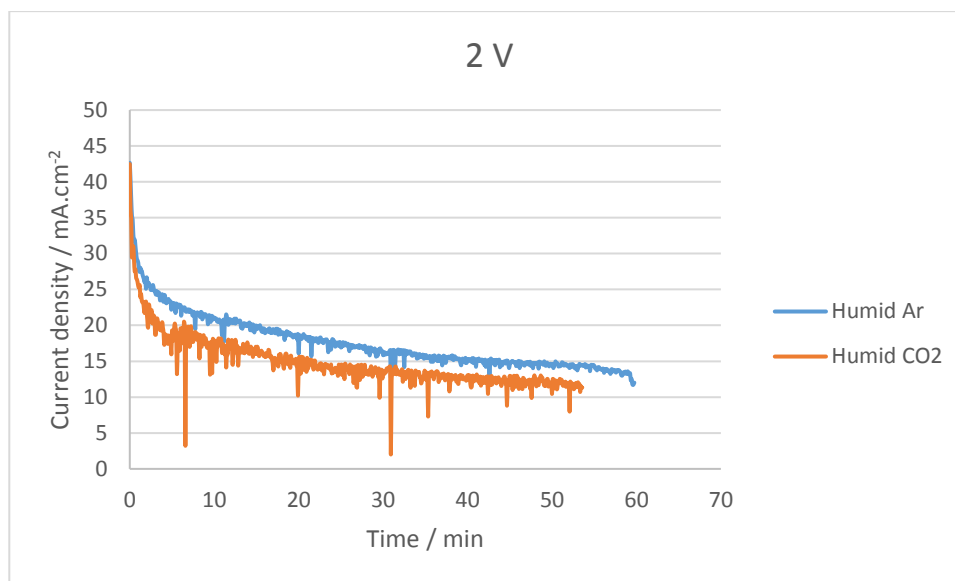


Figure 5.14. Current-time curves resulting from electrolysis performed in the KCl-LiCl molten chlorides with and without the introduction of CO₂ at 2V, 375 °C and 1.3 atm while employing design no.1 (the feed gas was kept continuously flowing over the molten salt).

Also, it can be noted that the current was slightly higher in the case where CO₂ gas was absent basically due to the obstruction of CO₂ gas against H₂O reduction on the graphite, particularly at high pressures though the possible reduction of CO₂ to CO₂²⁻ (reaction 5.15). This will be illustrated also in the next section describing a cyclic voltammetric analysis. Despite some spikes noticed in the blue curve in Figure 5.14, it can be seen that the drop of the curves in both cases was quite the same confirming the weak effect of CO₂ inside the molten chloride on this occasion. It has also been suggested that hydrogen evolution dominated during electrolysis with CO₂ slowing the rate of H₂O reduction.

2. The previous experiment was carried out using scale no. 3 as illustrated in Chapter 4 when the feed gas (97.9% CO₂ + 2.1% H₂O + 0% Ar) was continuously flowing at 10 mL/min through ceramic tubes at atmospheric pressure. Subsequently, the yield of fuel products collected from the cathodic tube changed significantly (Tables 5.4 and 5.5). This method of gas feed introduction was chosen as an appropriate way to increase CO₂ concentration and solubility (and thus reactivity) inside the molten chloride and collect the minimum rates of hydrocarbon products. In this case, titanium was used as an alternative metal for the cathode material.

Table 5.4. Cathodic product gas compositions and the current efficiency of the individual components after electrolysis in the molten chlorides at 1.5V and 375 °C (prior to carbonate ion formation).

Product	Gas product composition (Vol.%)	Uncertainty of gas composition	Production rate ($\mu\text{mol. cm}^{-2}.\text{h}^{-1}$)	Current efficiency (%)	Energy consumption (J)
H ₂	2.4	± 0.1	32	54.8	278
CH ₄	0.05	± 0.005	0.667	4.5	
CO	0	0	0	0	
CO ₂	34.8	--	----	----	
H ₂ O	2	----	----	----	
Ar	balance	----	----	----	

Table 5.5. Cathodic product gas compositions and the current efficiency of the individual components after electrolysis in molten chlorides at 2 V and 375 °C (including the event of carbonate ion formation).

Product	Gas product composition (Vol.%)	Uncertainty	Production rate ($\mu\text{mol. cm}^{-2}.\text{h}^{-1}$)	Current efficiency (%)	Energy consumption (J)
H ₂	2.48 (2.5)	± 0.1	19.1	28.2	311
CH ₄	0.05	± 0.005	0.385	2.3	
CO	0	0	0	0	
CO ₂	4.84	----	----	----	
H ₂ O	2	----	----	----	
Ar	balance	----	----	----	

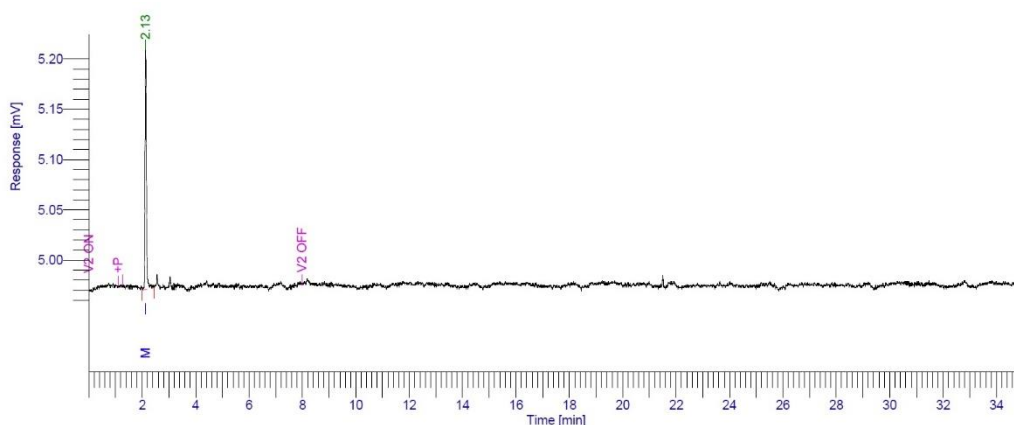


Figure 5.15. GC analysis of the hydrocarbon band for a cathodic gas product after electrolysis was performed in KCl-LiCl (41-59 mol%) molten salt at 2V and 375 °C (sample data was collected for the first 30 min prior to the event of carbonate ion formation).

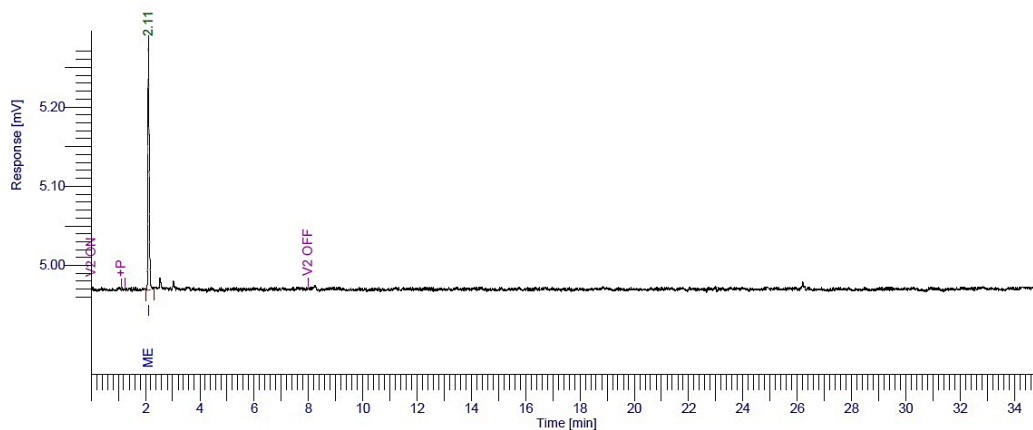


Figure 5.16. GC analysis of the hydrocarbon band for the cathodic gas product after electrolysis was performed in KCl-LiCl (41-59 mol%) molten salt at 2V and 375 °C (sample data was collected between 30-60 min after the start of the experiment, including the event of carbonate ion formation).

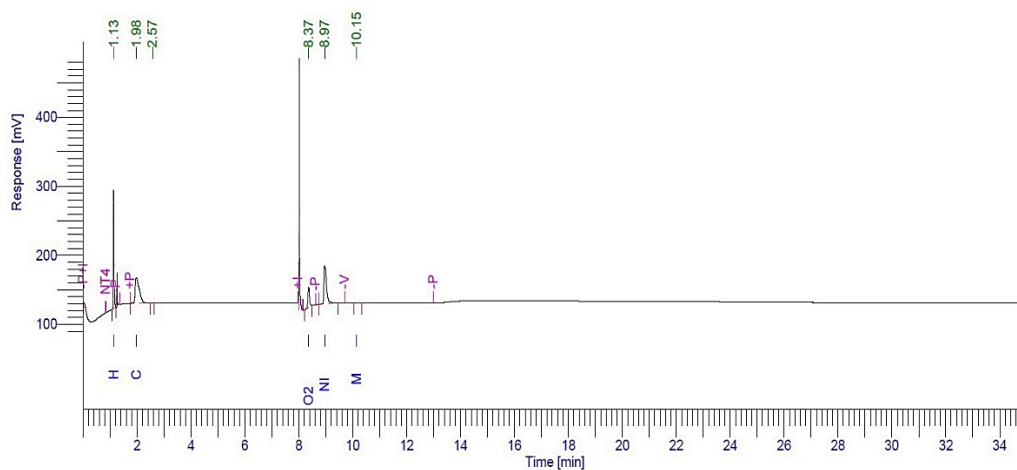


Figure 5.17. GC analysis of the non-hydrocarbon band for the cathodic gas product after electrolysis was performed in KCl-LiCl (41-59 mol%) molten salt at 2V and 375 °C (sample data was collected for the first 30 min prior to carbonate ion formation).

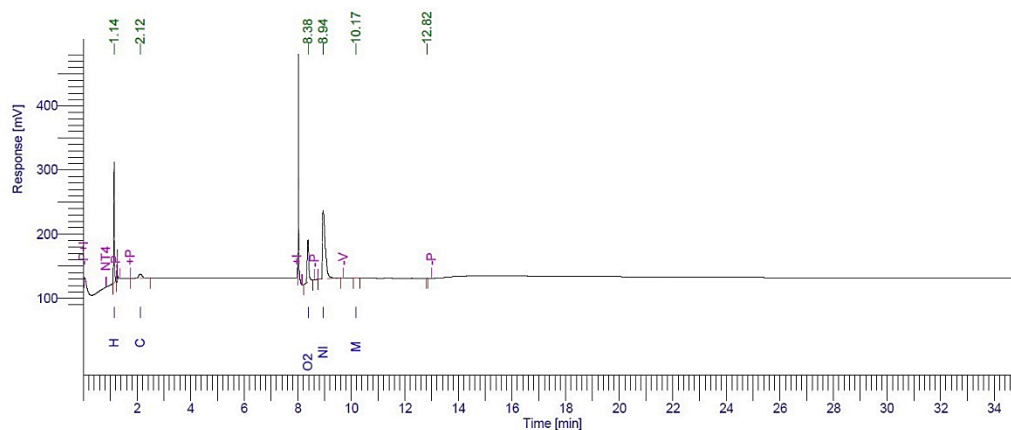


Figure 5.18. GC analysis of the non-hydrocarbon band for the cathodic gas product after electrolysis was performed in KCl-LiCl (41-59 mol%) molten salt at 2V and 375 °C (sample data was collected for 30-60 min, including the event of carbonate ion formation).

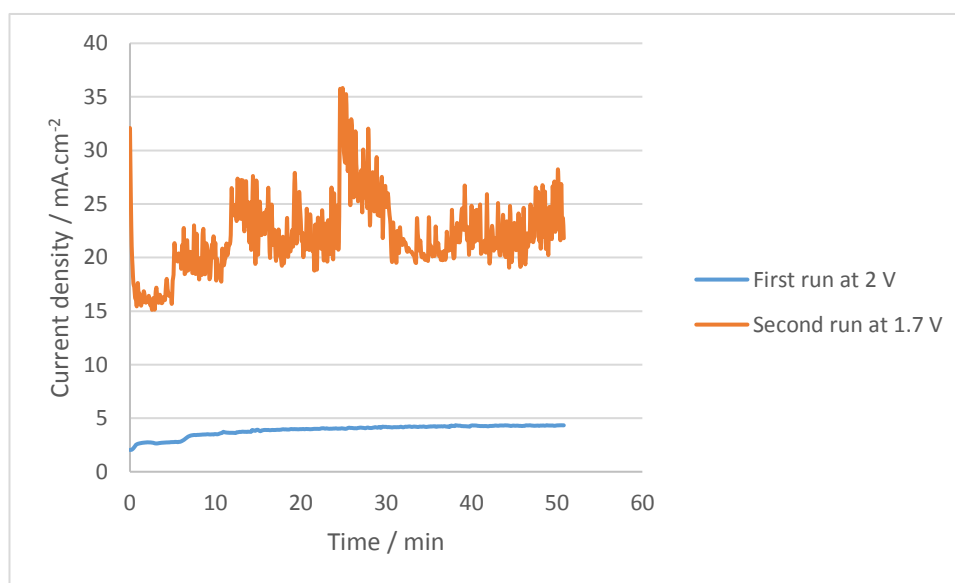


Figure 5.19. Current-time curves resulting from electrolysis performed in the molten chlorides at 375 °C and atmospheric pressure through employing design no.3 (the feed gas was kept flowing through the ceramic tube) on different occasions.

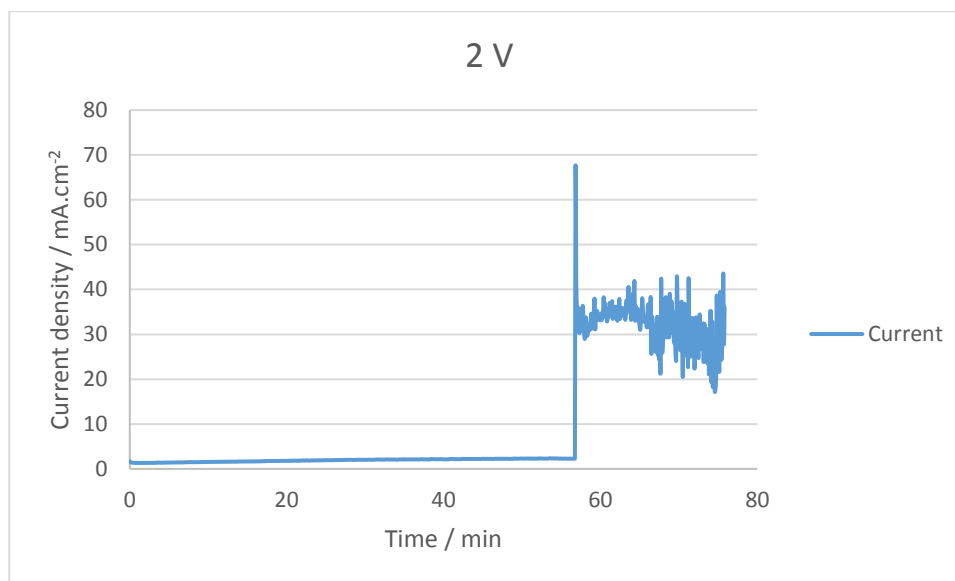


Figure 5.20. Current-time curves resulting from electrolysis performed in the molten chlorides at 375 °C and atmospheric pressure through employing design no.3 (the feed gas was kept flowing through the ceramic tube) for more than one hour at 2 V.

During the first one hour of the experimental run, it can be seen from Figure 5.19 that the resulting current increased slightly for 20 minutes during electrolysis and then remained stable at a level less than 100 mA. However, in the next one hour run, even at a lower applied voltage of 1.7 V, it can be noted that the current resulting from electrolysis was obviously higher than the previous hour because of CO₂ reduction to carbon and the presence of hydrocarbon gases in addition to H₂ (from H₂O reduction). The whole experiment was repeated for more than 60 min at 2 V to illustrate the situation including both currents explained above. It can be seen from Figure 5.20 that the recorded current remained at a lower level for less than 60 minutes, before beginning to rise up to 30 mA/cm² or higher. The rise of the current can be attributed to the evolution of carbon deposition on the cathode due to the reduction of carbonate ions which are considered as activated ions in molten

chlorides (Song, Xu et al. 2012). The formation of a carbonate ion can be justified in turn to be due to the reaction of CO₂ with OH⁻ generated in the molten chloride after the persistent reduction of H₂O as stated previously in reaction 2.83 (Kamali and Fray 2015).

Comparing GC results for the two occasions (Figures 5.15-18) as two gas samples were taken for the first 30 minutes and between 30 and 60 minutes for the last experiment, the following analysis can be noted:

1. The recorded peaks for H₂ and CH₄ in both cases seem to be identical (with minor differences such as the size of peak and accumulated traces of certain hydrocarbon species that were not specified in the GC). However, the concentration of both gases was higher in the first sample due to the higher amount of gas generation during the first 30 minutes of electrolysis as the electro-reduction of the carbonate ion (to carbon for instance) had not commenced yet. Thus, the reduction of H₂O to H₂ was not significantly affected. Nevertheless, the molar ratio of H₂/CH₄ produced was still approximately 50 in both cases.
2. The reaction of CO₂ with OH⁻ can be confirmed in the molten chloride for the second sample as the concentration of CO₂ reduced from 34.8% to 4.8% (Tables 5.4 and 5.5). Therefore, water vapour can play a significant role in this instance for CO₂ reduction (at atmospheric pressure) but not towards increasing hydrocarbon production unfortunately.
3. No CO can be detected in the molten chloride in both cases.

Comparing the gas product results from the cathode in the molten carbonate with the molten chloride, some remarks can be noted:

1. The molar ratio of H₂/CH₄ of product generated in the molten carbonates is about 24. This value is quite half of the ratio calculated for the molten

chlorides. This can be imputed to the higher possibility of hydrocarbon formation in the molten carbonates rather than in the molten chlorides. Therefore, CH₄ generation significantly, does not depend on only H₂ formation in the molten carbonate case.

2. The current efficiencies of both the H₂ and CH₄ products generated in the molten chlorides do not reach 60% on the best of occasions whereas the summation of current efficiencies of cathodic products in the molten carbonates can reach 95%. This can be imputed to the formation of CO in the molten carbonate case, increasing the opportunity of hydrocarbon formation. It can be concluded also that alkali metal deposition can occur slightly on the cathode in the molten chlorides for the first case (before CO₂ or carbonate ion reduction as seen in Table 5.4), in addition to the prospect of carbon deposition in the second case (after CO₂ or carbonate ion reduction as seen in Table 5.5).
3. The energy consumption was higher in the case of the molten chlorides compared with the molten carbonates even prior to the rise of the current during electrolysis in the molten chlorides due to reasons mentioned previously (Tables 5.4 and 5.5).

5.2.1 Cyclic voltammetry in molten chloride

The CO₂ effect in the molten chloride can also be detected using a cyclic voltammetry (CV) analysis in a three-electrode cell. Two graphite rods of 8 mm diameter were used as the working and counter electrodes respectively, whereas a nickel rod of 5 mm diameter was used as the quasi reference electrode in the molten chlorides KCl-LiCl of (41:59 mol%). CV was performed by a scan range from -2.7 to -0.75 V vs the Cl₂/Cl⁻ electrode at a rate of 100 mV/s. When CO₂ gas with a 200 mL/min flowrate was applied with 3% of the water vapour, it can be seen from Figure 5.21 that the main cathodic peak (C2)

was discharged starting at a potential of -2.4 V vs. Cl₂/Cl⁻. This was presumably due to the intercalation of lithium ions on the graphite electrode. There is a small peak (C1) at approximately -2 V that can be imputed to the reduction of CO₂ to CO₂²⁻ or CO (directly) by reactions 5.15 and 5.16 producing O²⁻ ions. These ions can lead to the formation of CO₃²⁻ which could be electro-reduced in turn to produce CO or carbon indirectly (Ijije, Lawrence et al. 2014). Therefore, the cathodic peak (C2) can involve the reduction of CO₃²⁻ in addition to lithium insertion.

In the reverse sweep of the scan on Figure 5.21, A2 and A1 oxidation peaks can be imputed to the stripping of lithium from the graphite cathode and the oxidation of the deposit carbon respectively. It can be noted that the electrochemical potential window between the onset potentials of peak C2 (-2.4 V) and A1 (-1.0 V) is about 1.4 V. The potential window is fairly close to the standard potential of -1.34 V vs. CO₃²⁻/O₂ calculated for the reduction of lithium carbonate to carbon (Ijije, Lawrence et al. 2014).

On the other hand, it has been claimed that between 390-480 °C, hydrogen adsorption can be found on a cathode in the molten chlorides at partial pressures of H₂O of up to 16 mm Hg. Using higher gas pressures of feed gas over the atmospheric levels would lead to an increase in the partial pressure of H₂O and the possibility of the hydrolysis reaction (2.55 or 2.57) occurring (White and Twardoch 1987). This is a process where hydrochloric acid gas (HCl) is not desired. It can be concluded from the above result that it would be difficult to produce C, CO and H₂ at the same time since higher pressures of CO₂ are required for C or CO formation.

Cyclic voltammetry cannot be performed while employing the introduction of scale no. 3 or any other design with a ceramic tube surrounding the electrodes.

This is because the movement of molten salt inside the tube occurs frequently causing current fluctuation and a peak interruption from the actual and incident potentials for oxidation and reduction products.

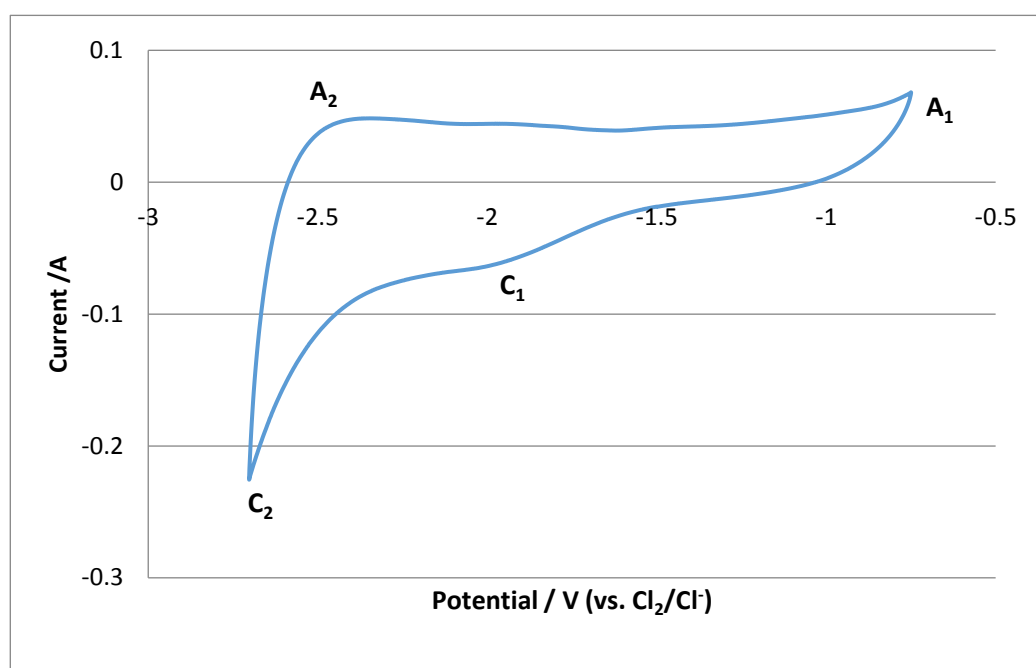


Figure 5.21. CV recorded from a graphite electrode on the molten chlorides KCl-LiCl at 375 °C with the application of CO₂ gas and H₂O.

5.3 Molten hydroxide

This kind of salt would be preferred in the case of hydrogen production. In this research, the work of electrolysis using this salt was included particularly for the sake of hydrocarbon formation. Hydrocarbon molecules can be formed

basically through a H₂ reaction with either C or CO as the same mechanism for molten chlorides. In most experiments using molten hydroxides, the conversion of CO₂ was very high but unfortunately the hydrocarbon yields were too low. This can be attributed generally to the reaction of CO₂ with hydroxide ions (reaction 2.83).

Therefore CO₂ must be diluted to lower concentrations by mixing with argon gas before introduction to the electrolyte, as this action can help reduce the reactivity of CO₂ with the salt, driving reaction (2.83) to the left side. The formation of carbonate ions can be reduced to provide enough time for the prospect of electro-reduction during electrolysis. However, CH₄ gas (for instance) can be formed by another way as follows:



Thus the abundance of hydrogen gas from rapid H₂O reduction in molten hydroxides can contribute towards driving reaction 5.18 through CH₄ formation. Moreover, if CO has been produced significantly from CO₂ reduction in the salt, other hydrocarbon molecules and in particular alkanes (such as C₂H₆ and C₃H₈), can be formed according to reaction 5.5 as stated previously.

Performing electrolysis with LiOH-NaOH (27-73 mol%) molten salt at 2 V applied voltage and at 275 °C with a gas feed (17% CO₂ + 3.1% H₂O by volume), it can be seen from Figures 5.22-23 and Table 5.6 that there is a distinct variation in the production rates. The H₂ production rate was 1.1 mmol/h.cm² whereas CH₄ was significantly lower at 1 μmol/h.cm² when the feed gas was maintained as flowing over the salt during electrolysis. Mild steel (5 mm diameter) and stainless steel (6 mm diameter) rods were used as cathode and anode metals respectively. The above outcome can be attributed to the weak reduction of CO₂ in the salt on this occasion. The hydrocarbon

production rate was significantly improved when the feed gas was kept bubbling inside the salt by a ceramic tube (10 mm ID, 50 cm long). It can be seen from the above table that the CH₄ rate increased largely this time from 1 to 6 μmol/h.cm² during the second run as CO₂ was promoted to dissolve in the salt. Therefore, the prospect of direct reduction of CO₂ to CO₂²⁻ and CO (reaction 5.15-5.16) respectively, can occur in the molten hydroxide. Surprisingly, at the same rate, the H₂ rate decreased from 1.1 mmol/h.cm² to just 185 μmol/h.cm², confirming the possible transformation of CO₂ or CO to hydrocarbons (Figures 5.24, 5.25). Hydrocarbon production inside the molten hydroxide can be confirmed actually by the existence of CO fuel with the cathode gas product. CO can be formed from CO₂ reduction by the steps mentioned in molten chloride experiments (reaction 5.15-16).

The scarcity of CO found in the cathodic products in both cases can be interpreted as follows:

1. This could be due to a lack of CO₂ reduction primarily in the molten hydroxide. Therefore, the formation of CH₄ was performed by the reaction of CO₂ with excess H₂.
2. The produced amount of CO during electrolysis in all cases was too little as CO can rapidly react with excess H₂ to produce CH₄.

Nevertheless as stated previously, the production of CH₄ gas as well as other hydrocarbons (alkanes and alkenes) can be performed from CO and H₂ by two methods: reactions 5.5-5.6 resulting in the formation of H₂O and reactions 5.7-5.8 resulting in the formation of CO₂.

Actually, reactions 5.7 and 5.8 (resulting in CO₂ generation) are thermodynamically more preferable because the free energies of reaction (ΔG_r) for both reactions are highly negative in comparison to reactions 5.5 and 5.6

(resulting in H₂O generation) particularly at lower temperatures according to the HSC software (version 6.12; Outokumpu Research). Moreover, CO₂ can be consumed or absorbed in the molten hydroxide to a larger extent than H₂O itself, shifting reactions 5.7 and 5.8 to the right hand side and thereby promoting hydrocarbon formation. The last idea can be supported also by the remaining amounts of CO₂ as a product as seen in Table 5.6. In addition to the unreacted amount of the gas, the existence of CO₂ in the gaseous product can be considered as another clue for hydrocarbon formation by the above reactions. Basically, as soon as the hydrocarbon molecule forms on cathode metal, the produced CO₂ bubbles find their way out with unreacted H₂ and CO besides the hydrocarbon bubbles themselves.

Nevertheless, the faradaic or current efficiency of H₂ in the first run shown in Table 5.6 was obviously very high as compared to the second run. This is due apparently because of the higher H₂ production rate in the first run. The resulting currents from both cases are still considerable as are expected by the literature (Divisek, Mergel et al. 1982).

On the other hand, hydrocarbon fuel efficiencies were too low obviously because of their lower production rates from the slow reduction of CO₂ to CO compared with rapid H₂ production.

The above experiments were repeated using a KOH-NaOH containing melt (50-50 mol%) at 220 °C and 2V applied cell voltage. Although the temperature used here was slightly lower than the one used for LiOH-NaOH molten salt, the results were quite the same regarding the production rates and faradaic efficiencies of H₂ and CH₄ in addition to CO₂ composition of the cathode product gas. This was despite the lower resulting current and the subsequent energy consumption in the case of KOH-NaOH molten salt (Table 5.7 and Figure 5.26).

Lastly, if the heating values or energy supplied from the produced fuels were comparable to or quite higher than the energy consumed while performing electrolysis, the process feasibility would be much better. This is because the yield of heat generated from the produced hydrocarbon (or fuel in general) can compensate for or substitute some of the normal electricity (or grid network) employed in large scale industry applications besides renewable energy. Nevertheless, the heating values from the produced fuels using molten hydroxide in general, are still far less than the required energy consumption because of the relatively large current consumed during electrolysis (Table 5.8).

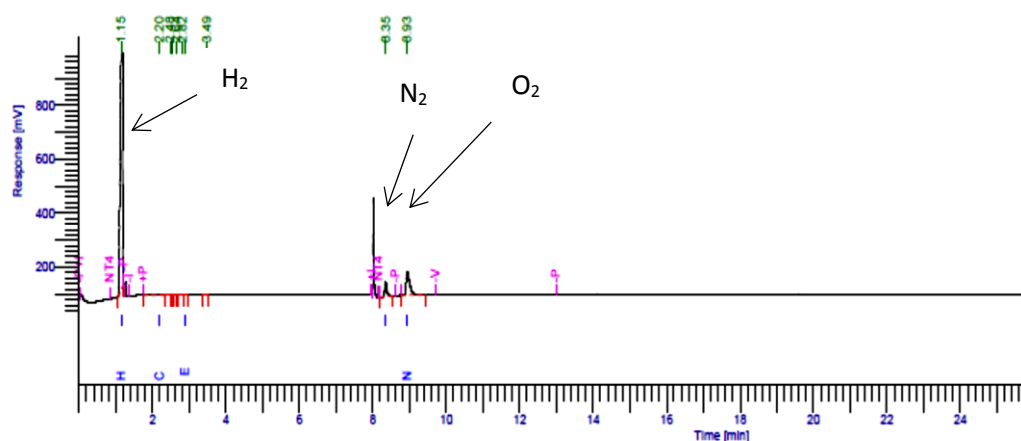


Figure 5.22. GC analysis of the non-hydrocarbon band for the cathodic gas product after electrolysis was performed in LiOH-NaOH (27-73 mol%) molten salt at 2V and 275 °C without gas feed submergence inside the salt and showing peaks for H₂, O₂, N₂. No peaks were detected for CO₂.

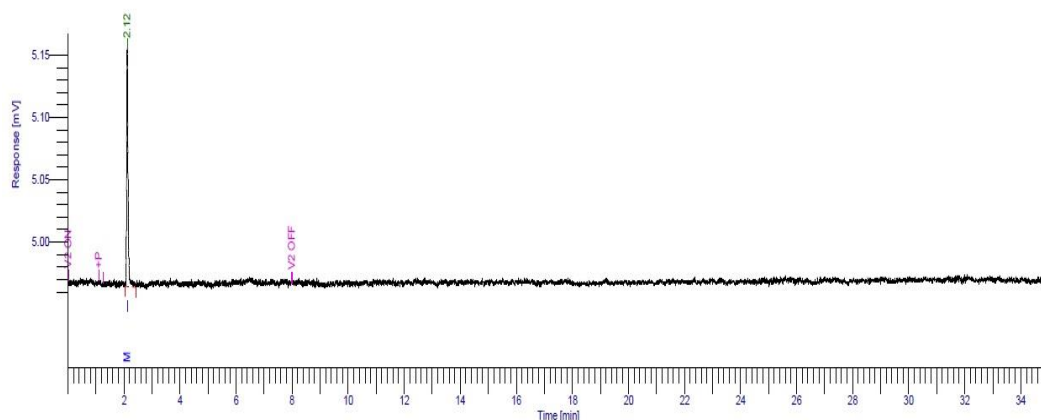


Figure 5.23. GC analysis of the hydrocarbon band for the cathodic gas product after electrolysis was performed in LiOH-NaOH (27-73 mol%) molten salt at 2V and 275 °C without gas feed submergence inside the salt and showing peaks for CH₄, C₂H₆ and C₃H₈.

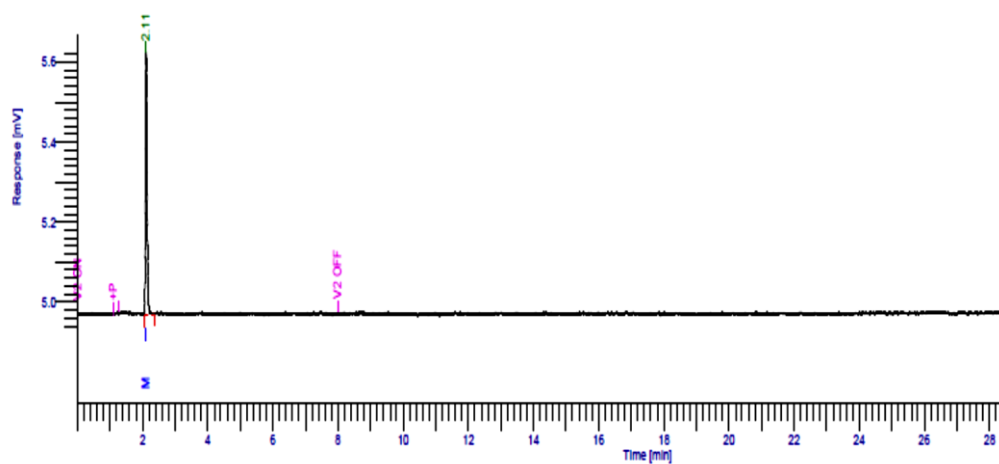


Figure 5.24. GC analysis of the hydrocarbon band for the cathodic gas product after electrolysis was performed in LiOH-NaOH (27-73 mol%) molten salt at 2V and 275 °C with gas feed submergence and showing peaks for CH₄ only.

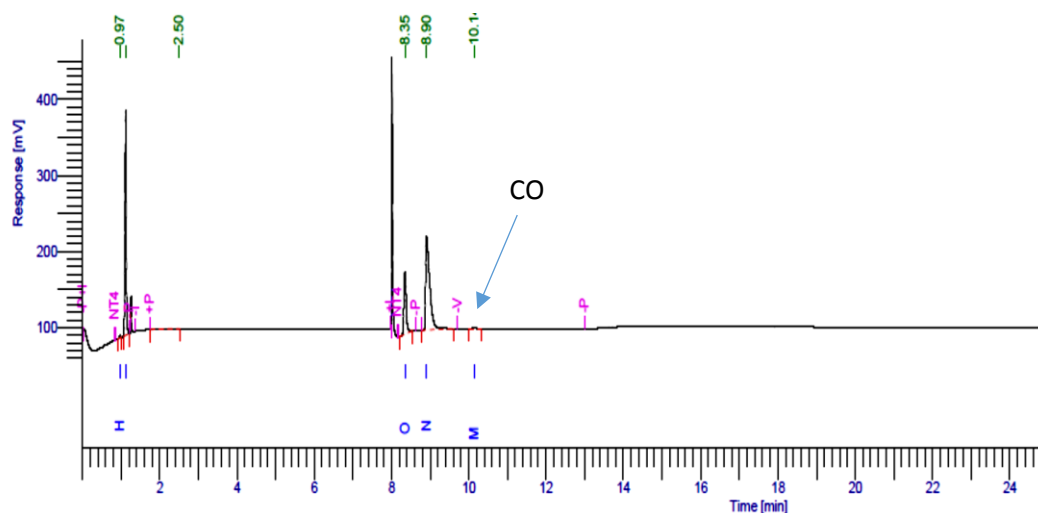


Figure 5.25. GC analysis of the non-hydrocarbon band for the cathodic gas product after electrolysis was performed in LiOH-NaOH (27-73 mol%) molten salt at 2V and 275 °C with gas feed submergence and showing peaks for H₂, O₂, N₂, CO₂ and CO.

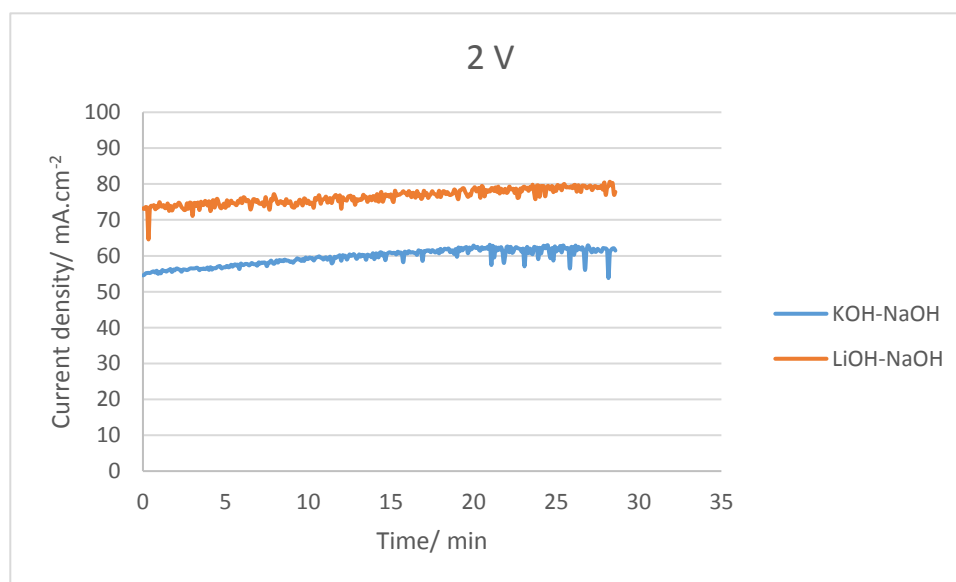


Figure 5.26. Current-time curves resulting from electrolysis performed in two different molten hydroxides at 2V.

Table 5.6: Cathodic product gas compositions and the current efficiency of the individual components during electrolysis in LiOH-NaOH (27-73 mol%) molten salt at 2V and 275 °C with and without gas feed tubing.

Run No.	Case	Product	Composition percentage in product (Vol.%)	Uncertainty of gas composition	Production rate ($\mu\text{mol.h}^{-1}.\text{cm}^{-2}$)	Current efficiency (%)
1	The feed gas was kept flowing over the salt.	H ₂	27.3	± 0.9	1142.8	87.3
		CH ₄	0.03	± 0.004	1.02	0.4
		CO	0	0	0	0
		CO ₂	0.48	----	----	----
		H ₂ O	0	----	----	----
		Ar	72.2	----	---	---
2	The feed gas was bubbling in the salt.	H ₂	4.44	± 0.1	185.7	13
		CH ₄	0.15	± 0.01	6.12	2
		CO	0	0	0	0
		CO ₂	0.75	----	-----	-----
		H ₂ O	0	----	----	---
		Ar	94.7	----	---	---

Table 5.7: Comparison of two sets of cathodic product gas compositions and the current efficiency of the individual components after electrolysis in two different molten hydroxides at 2V with gas feed tubing.

Molten salt	Temperature	Product	Composition percentage in product (Vol.%)	Uncertainty of gas composition	Production rate ($\mu\text{mol.h}^{-1}.\text{cm}^{-2}$)	Current efficiency (%)
LiOH-NaOH (27-73) Mol%	275	H ₂	4.44	± 0.1	185.7	13
		CH ₄	0.15	± 0.01	6.12	2
		CO	0	0	0	0
		CO ₂	0.75	----	----	----
		H ₂ O	0	----	---	---
		Ar	94.7	----	---	---
KOH-NaOH (50-50) Mol%	220	H ₂	3.94	± 0.1	164.7	15.6
		CH ₄	0.15	± 0.01	6.12	2.3
		CO	0	0	0	0
		CO ₂	0.58	----	----	----
		H ₂ O	0	----	---	---
		Ar	95.3	----	---	---

Table 5.8. Heating values and energy consumptions for H₂ and CH₄ production after electrolysis in two different molten hydroxides at 2V with gas feed tubing.

Molten salt	Temperature	Product	Production rate ($\mu\text{mol.h}^{-1}.\text{cm}^{-2}$)	Heating value (J)	Energy consumption (J)
LiOH-NaOH (27-73) Mol%	275	H ₂	185.7	130	1200
		CH ₄	6.12	14	
KOH-NaOH (50-50) Mol%	220	H ₂	164.7	116	1000
		CH ₄	6.12	12	

5.4 Summary

In this chapter, three different molten salt compositions were tested for the purpose of hydrocarbon production from the electrolysis of CO₂ and H₂O. The three categories were molten carbonates, chlorides and hydroxide salts. The lowest possible temperature was used in this chapter during the experiments as this is most preferred for hydrocarbon formation reactions.

For the molten carbonate mixture case, CO was found significantly in a higher production rate than H₂ for the cathodic gas product during electrolysis of ternary molten carbonates such as Li₂CO₃-Na₂CO₃-K₂CO₃ (43.5:31.5:25 mol%) associated with some hydrocarbon species such as methane and olefins mainly.

The justification of olefin formation rather than paraffin was preferred as the reaction of CO with H₂ is more feasible than in the case of paraffin production. The formation of hydrocarbons by this mechanism is more reasonable than the formation by the reaction of carbon with H₂ gas as carbon deposition rarely existed. The generation of hydrocarbons in general is more preferred where CO₂ was formed (from CO and H₂) instead of H₂O. The hydrocarbons in such a case can be extracted as higher types (C₂-C₅) in addition to CH₄. The priority

of olefin formation can be confirmed also by the mechanism of partial oxidation of methane. Due to the higher temperature medium, current efficiencies of hydrocarbon species in particular were higher in the molten carbonates than in the case of molten chlorides or hydroxides.

For the molten chloride case, the grounds for hydrocarbon formation were derived in the presence or absence of carbonate ions. However, no effect of CO₂ was found in the molten chlorides KCl-LiCl (41-59 mol%) using the scale no.1 design clarified in Chapter 4, even at 1.3 bar pressure of CO₂. Nevertheless, a minute amount of CH₄ (compared with H₂) was found using the scale no.3 design at atmospheric pressure. The employment of a higher H₂O content of feed gas should be avoided due to the formation of HCl gas in the product. From the cyclic voltammetry analysis, CO or carbon can be listed during the alkali metal deposition as the main reduction peak in the analysis.

For the molten hydroxide case, H₂ gas was rapidly produced from the reduction of H₂O during electrolysis despite tiny amounts of associated CH₄. CH₄ can be generated according to the reaction of CO₂ with abundant H₂. The hydrocarbon production rate can be increased by submerging the feed gas inside the molten salt using a ceramic tube.

Chapter 6

The Influence of Process Variables on the Production of Hydrocarbon Fuels.

Attention has largely centred in current times on the investigation of appropriate methods for CO₂ sequestration and conversion. The employment of molten salts as electrolytes in general can enhance the CO₂ conversion through electrolysis with or without the co-operation of water electrolysis. The justification of hydrocarbon generation has been already confirmed using different kinds of molten salts.

This chapter examines the effect of process variables including temperature, applied cell voltage and CO₂/H₂O ratio on the co-reduction of CO₂ and H₂O gases themselves and the production of hydrocarbons afterwards. Basically, various experiments of electrolysis were performed in the previous chapter using specific temperatures and cell voltages according to the available investigations regarding CO₂ and H₂O reduction and for the best conditions to justify hydrocarbon formation. However, performing electrolysis at different conditions is required due to the following reasons:

1. Different mechanisms can model hydrocarbon formation at different temperatures (for instance). The formation can be performed by the partial oxidation of methane for example at temperatures higher than expected for hydrocarbon formulation in general (by the direct combination of H₂ and CO).

The effect on molten salt properties should also be considered due to this alteration.

2. The final production of hydrocarbons in this research starts normally from the individual reductions of CO_2 and H_2O as subsequent reactions can be affected when electrolysis has already been performed at different conditions.

The study of the level of influence of each variable was divided into two sections for each kind of molten salt employed. Unfortunately, due to the limited time of this research in addition to the restricted process variables employed for molten chlorides such as electrolysis temperature, work on these salts for process variable studies was not implemented. On the other hand, titanium foil and stainless steel rod as mentioned previously, were used in this chapter as the cathode and anode material respectively.

6.1 Temperature

Basically, the variation of temperature in hydrocarbon formulation as for any chemical reaction in general, can affect the rate of reaction and the equilibrium position of the molecules produced reversibly during the hydrocarbon production process (reactions 5.5-8 for example). The effect of temperature will be studied in this research as the temperature itself was fixed during electrolysis due to the heating of the entire reactor by the furnace (Chapter 4). The effect of temperature can be very sensitive because of significant issues as explained previously. In molten carbonates for instance, temperature can be reduced to the lowest point as possible in order to maintain the salt in a liquid state on one side and for the sake of hydrocarbon formation preferred thermodynamically on the other side. However, the rate of this formation will essentially reduce at lower temperatures. Therefore, the primary choice of a

certain temperature for the entire process was done based on the ability of the salt for efficient electrolysis prior to successful hydrocarbon production. The temperature effect was studied in a molten carbonate and hydroxide but not chloride because of the substantially greater influence of H_2O on molten chlorides, particularly at high temperatures, as explained in chapters 4 and 5.

6.1.1 Molten carbonate.

The selectivity and production rates for various hydrocarbon species were investigated in molten carbonates at two different temperatures. Basically, the selectivity of the hydrocarbon species was calculated by the proportion of moles of the desired hydrocarbon species to the moles of the undesired products of H_2 and CO . The previous work of electrolysis at $425\text{ }^\circ\text{C}$ and 1.5 V using a gas feed of $48.4\% \text{ CO}_2 + 3.2\% \text{ H}_2\text{O} + 48.4\% \text{ Ar}$ composition was expanded to see the development of hydrocarbon formation at different higher temperatures. On this occasion, the surface area of the titanium plate cathode that was immersed in the salt, was 5.9 cm^2 .

Applying electrolysis at $500\text{ }^\circ\text{C}$, and as a consequence of increasing the resulting current as shown in Figure 6.8, it can be seen that the production rate of CO decreases by almost ten times the rate recorded during the run at $425\text{ }^\circ\text{C}$. Moreover, the slight decrease in the H_2 production rate can be attributed to the formation of a new hydrocarbon species (C_6H_{14} and particularly C_7H_{16}) as shown in Figures 6.2-6.5. Actually, C_7H_{18} was detected by the GC-mass spectrometric analysis as it cannot be confirmed through normal GC (Figure 6.2 and 6.3).

Table 6.1: Specification of the cathodic gas product during electrolysis of the molten carbonates at 1.5 V and 425 °C with the selectivity of hydrocarbons in the form of the gas composition obtained from GC analysis (H_2 , CO_2 and CO from TCD channel and CH_4 from FID channel).

Product	Gas product composition (Vol %)	Production rate ($\mu\text{mol.h}^{-1} \cdot \text{cm}^{-2}$)	Selectivity (%)	Current efficiency (%)	Heating value (J)	Energy consumption (J)
H_2	0.217	4.4	--	11.9	11.4	114.2
CH_4	0.056	1.1	6.8	12.5	10.4	
C_2H_4	0.04	0.8	5	13.2	12	
C_3H_6	0.025	0.5	3.1	12.7	11	
C_4H_8	0.026	0.5	3.1	17	14.5	
CO	0.58	11.7	---	31.8	35.3	
CO_2	52.7	----	---	----	----	
H_2O	2.4	----	---	----	----	
Ar	44	----	---	----	----	

It can be concluded at this point that the capability of water reduction (to H_2) can be enhanced by increasing the temperature in the molten carbonates despite the same or lower H_2 production rate than in the case of 425 °C. This enhancement can also hold true for the formation of relatively high molecular weight hydrocarbons (i.e. C_6H_{14} or C_7H_{16}) as will be justified later.

Table 6.2: Specification of the cathodic gas product during electrolysis on the molten carbonates at 1.5 V and 500 °C using GC analysis (H_2 , CO_2 and CO from TCD channel whereas CH_4 and C_2H_4 from FID channel) and mass spectrometric analysis (for C_7H_{16}).

Product	Gas product composition (Vol.%)	Uncertainty of gas composition	Production rate ($\mu\text{mol. cm}^{-2}.\text{h}^{-1}$)	Selectivity of hydrocarbons (%)	Current efficiency (%)	Heating value (J)	Energy consumption(J)
H_2	0.2	± 0.04	4	---	5.1	7.3	171
CH_4	0.02	± 0.006	0.4	7	2	2.6	
C_6H_{14}	0.12	± 0.01	2.4	42.1	58	75	
C_7H_{16}	0.061	± 0.003	1.2	21	32.4	43.3	
CO	0.1	± 0.01	1.7	----	2.2	3.7	
CO_2	40.3	----	----	----	---		
H_2O	3.1	----	----	----	--		
Ar	56.1	----	----	---	---		

It can be seen from Table 6.2 that the selectivity for different hydrocarbon species was relatively good at 425 °C and this enhanced (7-42% or 70% in total) at 500 °C due to the lower rates of H_2 and CO formation in the final product. Also, the formation of higher molecular weight products (i.e C_6H_{14} and C_7H_{16}) with small rates (2.4 and 1.2 $\mu\text{mol/h.cm}^2$ respectively) can offer a calorific heat value (heating value or the heat of combustion) by ten times the amount for H_2 or CO .

The increasing fuel production rates in general can be attributed also to the higher solubility of CO_2 in the molten carbonates at higher temperatures as attained from the higher current density recorded during electrolysis at 500 °C (Chapter 4). Therefore, the CO_2 content in the cathodic gas product was reduced during the second run of 500 °C (Tables 6.1, 6.2) (Figure 6.6).

The justification of fuel product formation from GC analysis

The identification of the H_2 peak and quantity from TCD analysis has been justified in previous chapters. Nevertheless, the identification of the H_2 peak in the mass spectrum could not be found because the gas is basically lighter than the carrier gas (which is helium).

CO gas was found albeit in the TCD analysis from GC by a tiny peak seen in Figure 6.6. This peak was confirmed for CO as it matches with the same peak at 9.3 minute retention time of the TCD analysis when the standard gas was analysed to calibrate with GC in the same day (Figure 6.7 and Table 3.4).

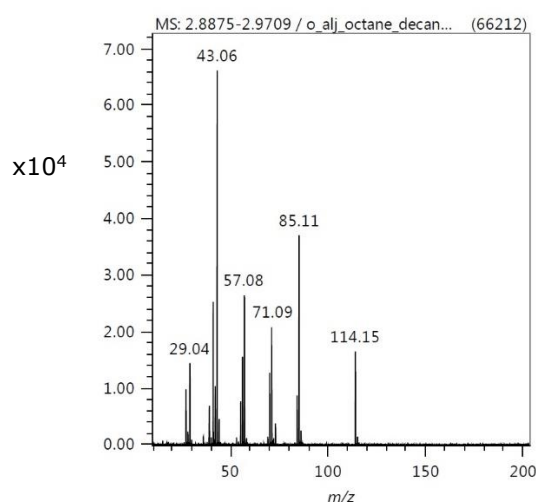


Figure 6.1. Mass spectrum of C_8H_{18} standard (mixed with dichloromethane) eluting at approximately 3 minute from GC.

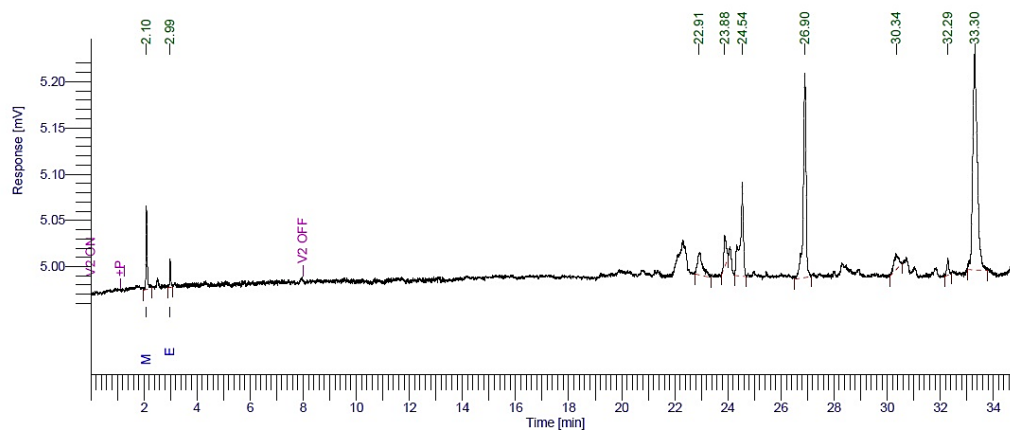


Figure 6.2. FID detector analysis of a cathodic gas sample taken during the electrolysis of the molten carbonates at 1.5 V and 500 °C obtained from Elmer GC (run1).

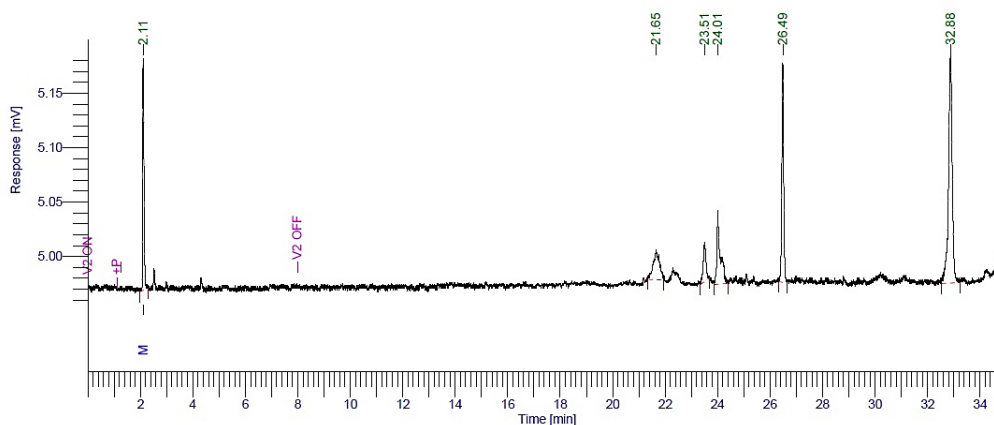


Figure 6.3. FID detector analysis of the cathodic gas sample taken during electrolysis in the molten carbonates at 1.5 V and 500 °C obtained from Elmer GC (run2).

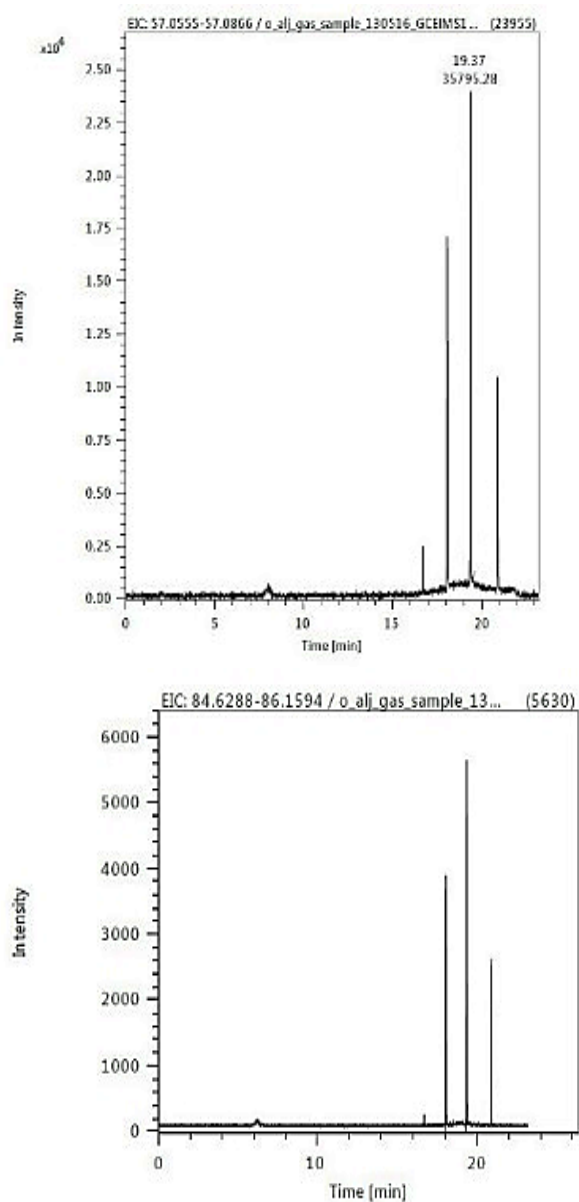


Figure 6.4. Extracted analysis of peak 85 (bottom) and peak 57 (top) from the total ions of the gases eluting from the GC before the fragmentation in mass spectrometry from the gas sample taken during electrolysis of the molten carbonates under 1.5 V at 500 °C and gas feed composition of $\text{CO}_2/\text{H}_2\text{O}=15.6$.

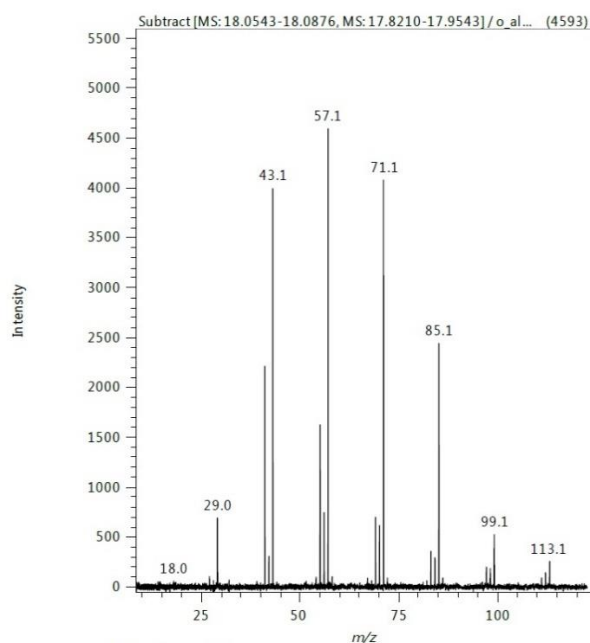


Figure 6.5. The mass spectrum of compounds eluting at approximately 18 min in MS-GC after injection from the gas sample taken during electrolysis on the molten carbonates under 1.5 V at 500 °C and gas feed composition of $\text{CO}_2/\text{H}_2\text{O}=15.6$.

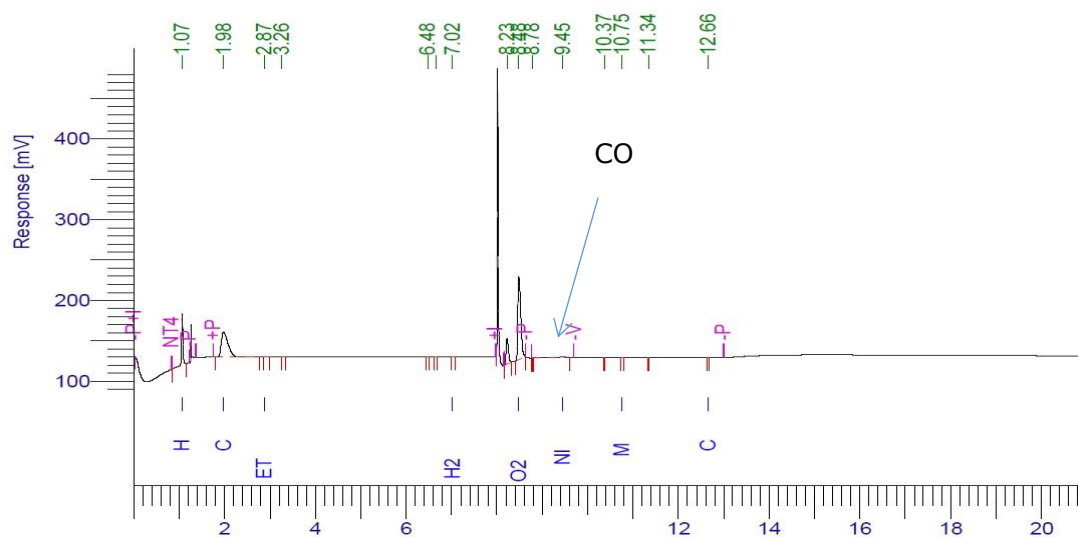


Figure 6.6. TCD detector analysis of the cathodic gas sample taken during electrolysis at 1.5 V and 500 °C as obtained from Elmer GC.

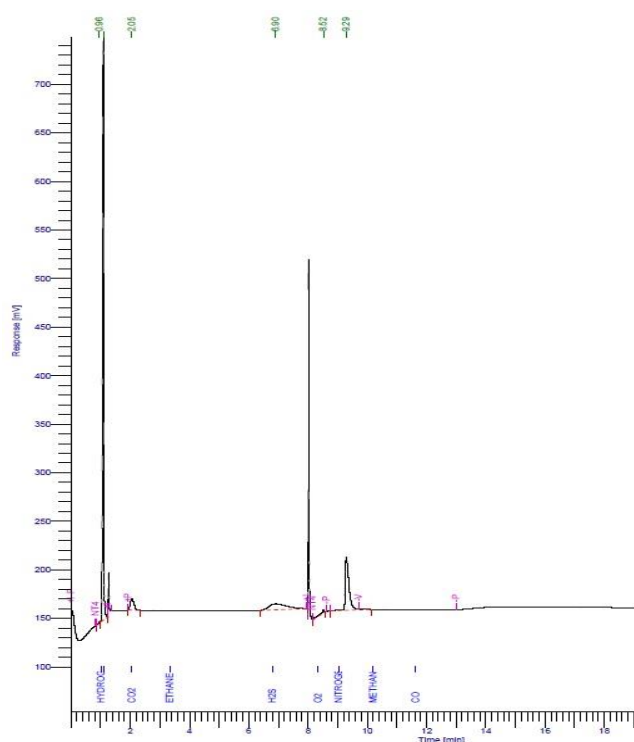


Figure 6.7.: TCD detector analysis of the standard permanent gas (containing 10% H_2 , 10% CO_2 and 40% CO) from GC.

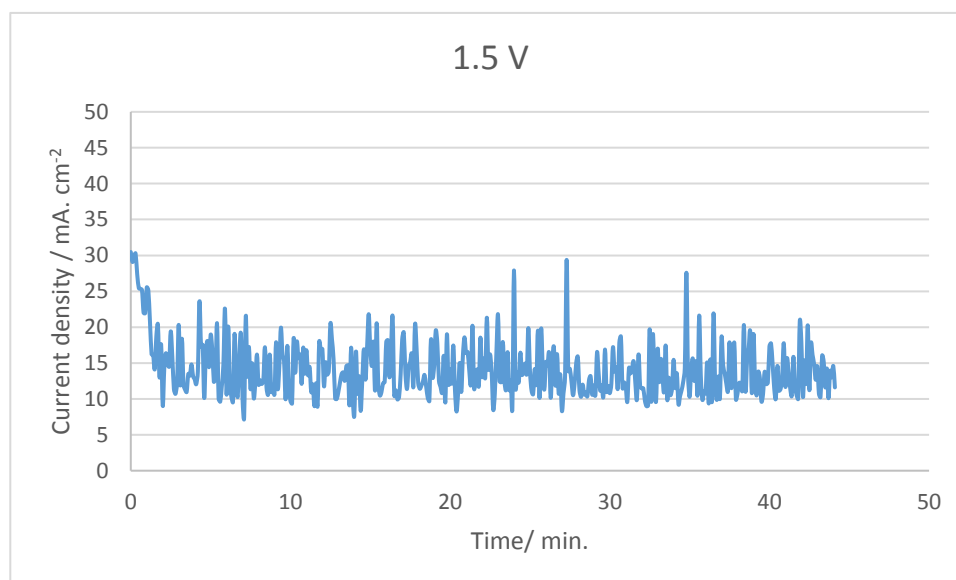


Figure 6.8. Current-time curves resulting from electrolysis performed in molten carbonates at 1.5 V and 500 °C.

The peak was shifted clearly as seen earlier from the retention time marked for CO (in both the standard and gas sample analyses) by the software as shown in the Figure due to the delay in the second column in channel B specified for permanent gas analysis (Figures 6.6-6.7).

At least three or four products of hydrocarbons (with a higher molecular weight than C_6H_{14}), can be confirmed already by the peaks shown in the mass spectrometry analysis with different retention times during electrolysis at a CO_2/H_2O ratio of 15.6 for the feed gas (Figure 6.4). Each peak shows the same behaviour for the mass spectrum when it has been analysed individually and the spectrum can be matched for the hydrocarbon product of C_8H_{18} (or over) (Figure 6.5).

The analysis of the mass spectrum (Figure 6.5) can confirm the identity of hydrocarbons higher than C_8 products (such as C_9H_{20} or $C_{10}H_{22}$) from the clear fragments lost from the last specified hydrocarbon during the analysis (43, 57, 85, 99 and 113). However, as no clear peak of an even number was shown after fragment 113, the products were assigned to C_6H_{14} and C_7H_{16} for more certainty. This certainty can be confirmed from the FID analysis for another gas sample taken from the same experiment (Figure 6.2). Two prominent peaks were shown between the 26 and 34 minute retention times on the chromatogram as they could not be identified previously from the GC analysis alone. These peaks can be assigned for C_6H_{14} and C_7H_{16} as compared with the corresponding FID analyses in the other sections in this chapter (Figure 6.18 for instance) and identified by MS analysis. Interestingly, the last two peaks in question exhibit the same retention times as shown on the FID analysis of another gas sample taken from a separate experiment of the same case (process variables) (Figure 6.3).

Table 6.3. List of $\Delta_r G$ and $\Delta_r H$ for the generation of some hydrocarbon products from the Fischer-Tropsch reaction (CO_2 or H_2O formation) and partial oxidation of methane at 500 °C. HSC Chemistry Software (version 6.12; Outokumpu Research).

Product	Fischer-Tropsch Reaction				CH ₄ partial oxidation	
	ΔG (KJ.mol ⁻¹)		ΔH (KJ.mol ⁻¹)		ΔG (KJ. mol ⁻¹)	ΔH (KJ. mol ⁻¹)
	<i>CO₂ formed</i>	<i>H₂O formed</i>	<i>CO₂ formed</i>	<i>H₂O formed</i>		
CH ₄	-40.29	-29.9	-258.59	-221.37	---	----
C ₂ H ₆	-9.68	11.10	-446.82	-372.37	-134.1	-175.7
C ₂ H ₄	30.28	51.06	-303.79	-229.35	-299.2	-278.8
C ₃ H ₈	14.43	45.59	-525.5	-413.87	-274.7	-241.9
C ₃ H ₆	38.15	69.31	-386.19	-274.53	-456.0	-348.7
C ₄ H ₁₀	28.53	70.08	-684.90	-536.01	-425.3	-388.8
C ₄ H ₈	55.74	97.29	-710.86	-561.97	-603.1	-660.9
C ₅ H ₁₂	54.87	97.31	-1037.57	-609.94	-563.7	-729.0
C ₅ H ₁₀	80.07	132.0	-907.92	-721.82	-743.5	-845.4
C ₆ H ₁₄	72.68	135.0	-1058.63	-835.3	-886.2	-1030.0
C ₆ H ₁₂	102.18	152.06	-1104.99	-696.53	-710.6	-737.5
C ₇ H ₁₆	81.43	154.14	-1219.94	-959.38	-866.6	-886.4
C ₇ H ₁₄	124.29	197.0	-1302.07	-1041.52	-1028.8	-1214.6

The theoretical justification of C₇H₁₆ formation

For the conventional formation of C₇H₁₆ (for instance) by the Fischer-Tropsch process, numerous moles of CO and H₂ need to be involved to formulate the final compound as follows:



By employing the same mechanisms as explained in Chapter 5, it is clear that the formulation of C_7H_{16} from the partial oxidation of methane is more feasible as the formation of CH_4 itself is still possible at temperatures as high as 500 °C (see Table 6.3).

Therefore, the provision of large molecular weight hydrocarbon formation can be justified now at elevated temperatures according to the same mechanisms as illustrated in Chapter 2. In the beginning, hydrocarbon formation in general can behave like carbon deposition in terms of the process variables during CO_2 reduction in molten carbonates. Therefore, process variables affecting carbon product from the CO_2 sole conversion (without H_2O) can act as a sequential effect on hydrocarbon formation after H_2O addition. It has been found that temperature has an important influence on the morphology and particle size of deposited carbon (Tang, Yin et al. 2013). The particle size of carbon can increase with increasing electrolysis temperature and result in carbon deposition that will be denser (although not quicker).

The existence of C_2H_4 (even in a tiny peak) as an olefin beside a paraffin (alkane) at high temperatures (as shown in Figure 6.2) can justify the formation of a large hydrocarbon like C_6H_{14} or C_7H_{16} through a process following the steps in reactions 2.64-67 (Groggins 1958).

Thus a paraffin like propane can be normally alkylated at high temperatures even in the absence of catalysis according to the previous steps composed of free radicals like isopropyl radical (2.65). The reaction of isopropyl radical with an olefin (2.66) and paraffin (2.67) molecule will produce larger alkylated products. The polymerization of olefins to higher molecular weight hydrocarbons can also occur if the olefin content in the product has increased.

Indeed, the methyl radical ($\text{CH}_3^\bullet$) can also be formed by the partial oxidation of methane as performed in the molten carbonates as a perfect medium for oxide ion transformation through the mechanism explained before (reactions 2.61-63). The methyl radical then continues to attack other paraffins like C_3H_8 and produce longer straight chain hydrocarbons or even branched hydrocarbons at this stage. It can be noted that the branched or isomer alkanes can be more easily formed rather than straight chain types in the presence of olefins in the product (Groggins 1958). Moreover, the formation of lower hydrocarbon species from C_2 to C_4 will also be lower at this stage. The proportion of the CO_2 to H_2O mole ratio will affect the formation of large molecular weight species of hydrocarbons as will be illustrated later in this chapter.

Finally, it is worthwhile to note that performing the electrolysis at higher temperatures ($> 500\text{ }^\circ\text{C}$) will not lead to the possible formation of hydrocarbons due to the lack of CH_4 formation in general.

6.1.2 Molten hydroxide

Although gas product specification results were basically found to be better at low temperatures, the electrolytic temperature in the molten hydroxide was increased to see the improvement of fuel production, while the undesired, rapid carbonate ion formation (2.83) from the CO_2 reaction with the salt has been reduced.

The negative (Δ_rG) energy of the last reaction can decrease and become even more positive by increasing the temperature shift for the reaction to the left side and decreasing carbonate ion formation (HSC Chemistry software Version

6.12; Outokumpu Research). Basically halting this reaction can then contribute to clear electrolysis and thus successful hydrocarbon formation. Table 6.4 illustrates the effect of temperature on the production rates of H₂, CO and CH₄ during the electrolysis of LiOH-NaOH molten salt at 2V cell voltage using the same gas feed composition of CO₂, H₂O and Ar employed during a 275 °C run in Chapter 5. KOH-NaOH salt was used in the case of the 220 °C run because its melting point at 187 °C is lower than that of the LiOH-NaOH eutectic mixture.

Table 6.4: Specification of the cathodic gas product during electrolysis in the molten hydroxides at 2V and different temperatures where the gas composition has been obtained from GC analysis (H₂, CO₂ and CO from TCD channel and CH₄ from FID channel).

Molten salt	Temperature	Product	Composition percentage in product (vol%)	Uncertainty of gas composition	Production rate (μmol.h ⁻¹ . cm ⁻²)	Current efficiency (%)
KOH-NaOH (50-50) mol%	220	H ₂	3.94	± 0.1	164.7	15.6
		CH ₄	0.15	± 0.01	6.12	2.3
		CO	0	0	0	0
		CO ₂	0.58	----	---	---
		H ₂ O	0	----	--	--
		Ar	95.3	----	---	---
LiOH-NaOH (27-73) mol%	275	H ₂	4.44	± 0.1	185.7	13
		CH ₄	0.15	± 0.01	6.12	2
		CO	0	0	0	0
		CO ₂	0.75	---	---	---
		Ar	94.7	---	---	---
LiOH-NaOH (27-73) mol%	335	H ₂	1.00	± 0.05	41.6	1.6
		CH ₄	0.02	± 0.006	0.8	0.13
		CO	0.02	± 0.007	0.8	0.03
		CO ₂	0.42	----	--	--
		H ₂ O	1.1	----	--	--
		Ar	97.4	----	--	--

It can be seen from Table 6.4 that the H₂ production rate became slightly higher when the electrolysis temperature increased from 220 °C to 275 °C at the same applied voltage and then dropped significantly at a lower level of 42 μmol/h at 335 °C. However, the rates for CO and CH₄ were kept at the same levels when temperature increased from 220 °C to 275 °C and then inclined gradually to 0.8 μmol/h for both fuels at 335 °C.

It has been suggested that increasing the electrolytic temperature does not significantly improve hydrocarbon, H₂ or even CO production in molten hydroxides. It was also found that H₂O solubility in the molten hydroxide is affected by Henry's law (Hoyt 1967):

$$P_{H_2O} = k N_{H_2O} \quad (6.4)$$

Where P_{H_2O} is the partial pressure of H₂O in the feed gas, k is Henry's constant (atm. mol⁻¹. Kg) and N_{H_2O} is the amount of H₂O dissolved in melt (mol. Kg⁻¹).

Temperature dependence of Henry's constant is given by the relation (Tomkins and Bansal 2016):

$$\ln k = 10.8 - 8081/T \quad (T \text{ in Kelvin}) \quad (6.5)$$

Therefore, the constant k is higher at increased temperatures and in contrast, N_{H_2O} will be lower or, in other words, the solubility of H₂O will be lower. As a result, the formation of the carbonate ion (or the reactivity of CO₂) should be higher when driving reaction 2.83 to the right hand side. This effect can be confirmed in the result by the lower CO₂ content in the cathodic gas product in Table 6.4 at 335 °C. The formation of H₂ and CH₄ will decrease significantly because of the last action.

However, as CO had been produced (even in a minor quantity) in the last run of 335 °C, this can be a clue to confirm the following statements:

1. The reduction of CO₂ to CO can occur in the molten hydroxide (at least by a low rate) (Figure 5.25).
2. The formation of hydrocarbons in general (particularly at 220 and 275 °C) can be confirmed from the reaction of CO with H₂ (more feasible than the respective formation from CO₂ with H₂) as the tiny amounts of CO can be transferred ultimately to CH₄ by the excess amounts of H₂ in the cathodic gas product.

Nevertheless, alkali metal deposition (reaction 2.82) can instead be the predominant cathodic reaction at electrolytic temperatures higher than 275 °C (and at a lower H₂O content in the salt possibly) consuming higher energy and reducing the current efficiencies (Table 6.4) while H₂O reduction has diminished by this stage.

Meanwhile, H₂ can be produced at a high rate in the case of sole H₂O submission (without CO₂) in the molten hydroxide as follows:



However, the current efficiency at this stage also will be reduced as H₂ was formed after metal deposition. Nevertheless, at the stage where CO₂ was engaged, the solubility of H₂O was not sufficient (as confirmed) to perform the last reaction due to carbonate ion formation in the molten hydroxide.

Regarding CO₂ conversion itself, it can be noticed that CO₂ composition in the gas product, which is obtained due to the unreacted (or by-product) CO₂ with the product, decreased quite significantly from 0.75% to 0.42% when the temperature was raised from 275 °C to 335 °C. However, the reacted amount

of CO_2 could not be transferred significantly to CO or hydrocarbon species obviously because of the prospects chemi-sorption of CO_2 in the molten hydroxides as stated before.

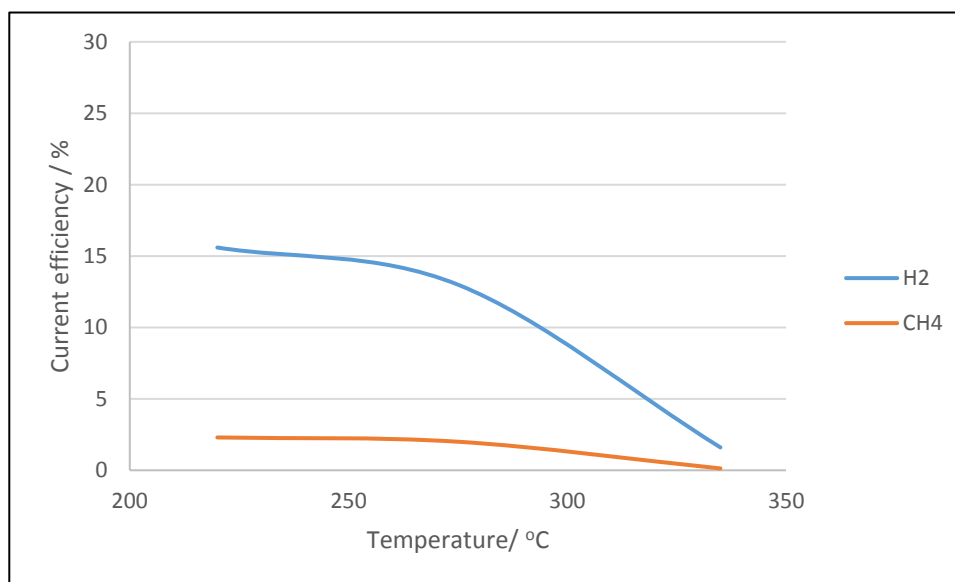


Figure 6.9. The plots of current efficiency of the indicated fuel species with electrolytic temperature in the molten hydroxides under a cell voltage of 2V.

Moreover, the current efficiencies of H_2 and CH_4 produced did not present any progress as justified previously. It can be clarified from Figure 6.11 that the values of efficiencies started as 15.6 and 2.3% for H_2 and CH_4 respectively at 220 °C and then decreased slightly at 275 °C, and then to a larger extent at 335 °C because of alkali metal deposition as stated before.

6.2 Applied cell voltage

In general, the molten salts used in this research have both high thermal and electrochemical stability when various cell voltages are applied particularly at the adjusted gas feed composition before the event of alkali metal deposition on the cathode.

Actually, the cell voltage is a key variable that can affect energy consumption or current efficiency but it can also improve the product properties at the same time (Tang, Yin et al. 2013).

If solid accumulation (carbon or alkali metal) was kept as low as possible on the cathode or inside the molten salt during electrolysis at cell voltages higher than the ones employed in the previous experiment, fuel gas products would be produced at higher rates on one side with plausible current efficiencies on the other side.

6.2.1 Molten carbonate

The effect of the applied cell voltage on carbon deposition in the molten carbonates has been confirmed in the literature. Employing higher cell voltages (than 2 V as confirmed for carbon deposition) through the range of 4 to 6 V, can improve the particle size of deposited carbon but not always result in an increase in the deposition rate itself (Ijije, Sun et al. 2014). Even so, rapid carbon deposition in the molten carbonates will not be preferred for the sake of hydrocarbon formation. Therefore, the cell voltage used in this salt was kept as low as 1.5 V to avoid carbon and alkaline metal deposition that can otherwise commence at 2 V. It was found that the cell voltage of 1.5 V in the molten carbonates is more sufficient to carry out electrolysis (Yin, Mao et al. 2013) for CO₂ and H₂O individually to CO and H₂, prior to the feasible formation of CH₄

or hydrocarbons in general. To show the effect of a 2 V cell voltage though, Figure 6.12 illustrates the high difference between the average current resulting from electrolysis applied at 1.5 V where hydrocarbon formation was confirmed and the current from the 2 V run, where carbon deposition occurred. While both runs were performed at 425 °C and with the same gas feed composition, hydrocarbon formation at 2 V was rare and not noticeable. However, some of the hydrocarbon species (such as CH₄, C₂H₄ and C₃H₆) found in the FID results of the last experiments (425 or 500 °C run at 1.5 V) were still shown slightly in the FID result of the 2 V run at 500 °C at least with quite low contents and production rates (Figure 6.13). This can generally confirm (or match) the results of hydrocarbon formation as previously stated for further certainty. The spikes shown in current curve in the 1.5 V case in Figure 6.12 can be attributed to the formation of gas bubbles produced on either or both the anode and cathode, whereas the formation of CO, H₂ and hydrocarbons is still feasible. It is worthwhile to say then that hydrocarbons, CO and H₂ can be formed on the cathode at high temperatures and under a cell voltage of 2 V where carbon deposition is not quick enough on the cathode (Tang, Yin et al. 2013) to feasibly generate the above species as illustrated in the previous section.

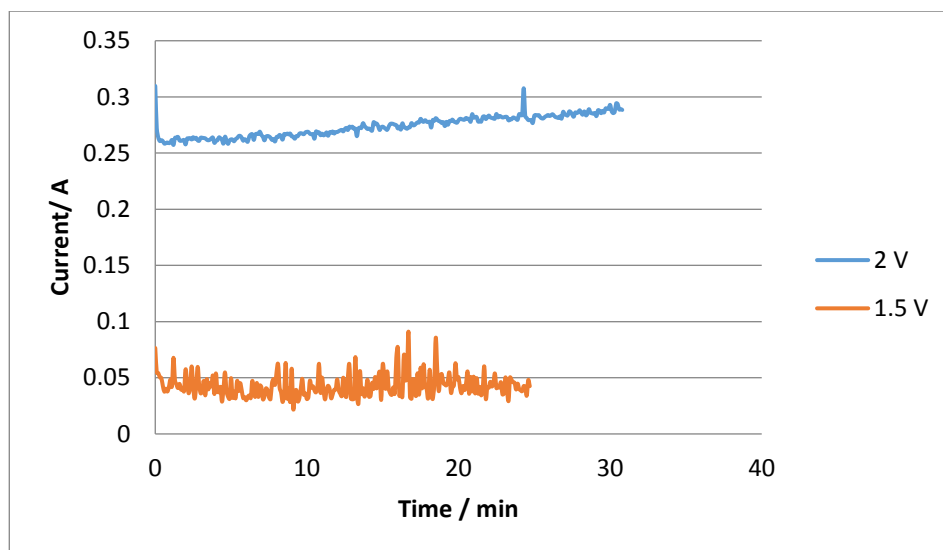


Figure 6.10. Current-time plots of electrolysis in the molten carbonates at 500 °C under the indicated cell voltage.

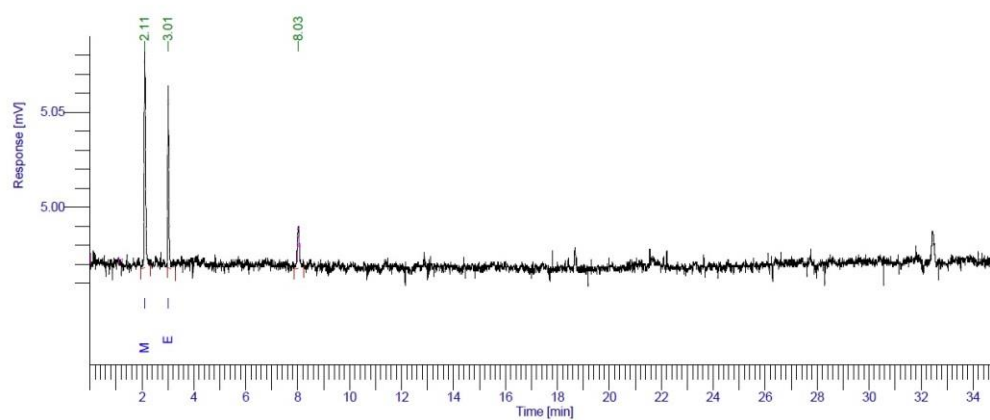


Figure 6.11. FID detector analysis of the cathodic gas sample taken during electrolysis in the molten carbonates at 2 V and 500 °C, obtained from Elmer GC.

6.2.2 Molten hydroxide

The situation was quite different for the molten hydroxide. When the applied cell voltage in LiOH-NaOH salt electrolysis was raised from 2 to 3 V, the production rates of CH_4 increased dramatically by 200% despite the high resulting current observed in Table 6.5 and Figure 6.14 for 3 V cell applied voltage. Actually, the rise of CH_4 production rates as well as the generation of CO in the second run of 3 V, can be counted as further evidence for CO_2 reduction in the molten hydroxides as the production rate of H_2 decreases by half of the value obtained in the 2 V run. The mitigation of the H_2 rate suggests the rapid formation of CO and CH_4 from CO_2 reduction with the possible electrodeposition of alkali metal at a high cell voltage, consequently affecting the current efficiencies of the products.

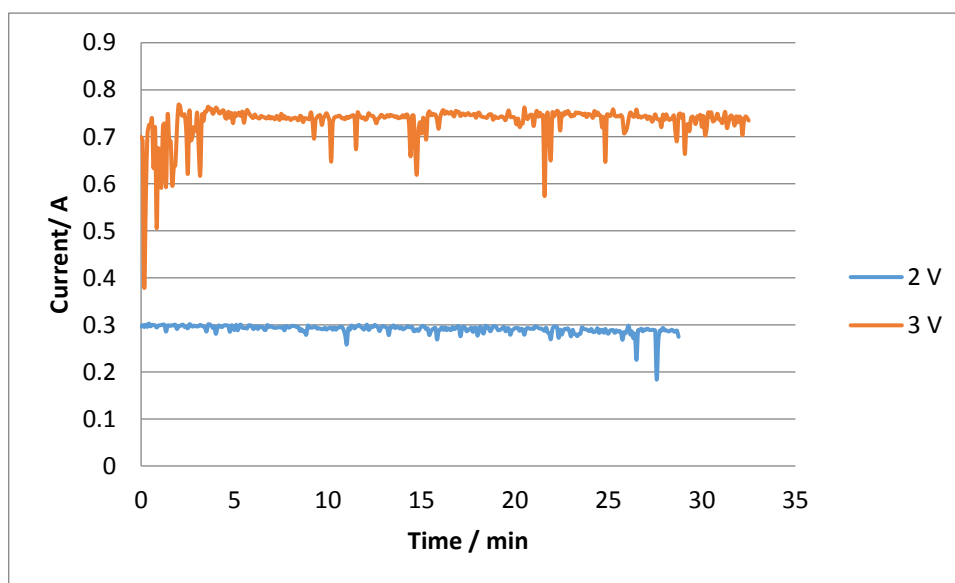


Figure 6.12. Current-time plots of electrolysis in the LiOH-NaOH (27-73) Mol% molten salt at 275 °C under the indicated cell voltage.

Table 6.5: Specification of cathodic gas product during electrolysis in the LiOH-NaOH molten hydroxide at 275 °C under 2 and 3 V of cell voltage where the gas composition was obtained from GC analysis (H_2 and CO from TCD channel and CH_4 from FID channel).

Run	Cell voltage (V)	Temperature (°C)	Product	Composition percentage in product (Vol.%)	Uncertainty of gas composition	Production rate (mmol. h ⁻¹)	Current efficiency (%)
1	2	275	H ₂	4.44	± 0.1	185.7	13
			CH ₄	0.15	± 0.01	6.12	2
			CO	0	0	0	2.3
2	3	275	H ₂	2.25	± 0.05	93.9	3.1
			CH ₄	0.5	± 0.05	20.4	1.4
			CO	1.43	± 0.04	0.3	2

The predominant formation of CH₄ or (in general) alkane formulas rather than other kinds of hydrocarbons is because of the lack of possibility of methane partial oxidation in a molten hydroxide in contrast with molten carbonates and chloride mediums. As previously stated that peroxide ions (O₂²⁻) are largely responsible for partial oxidation in molten salts, the formation of this type of reactive oxides unfortunately was quite absent in the molten hydroxide due to the acidic nature of the salt, even in the presence of minor amounts of H₂O.

6.3 CO₂/H₂O ratio

This ratio is one of the most important variables in the process. Actually, it has been considered due to the prospective effect of CO₂ and H₂O reduction if they proceed individually before the complete formation of hydrocarbons. Generally, the more the H₂O content in a feed gas (or less CO₂/H₂O ratio), the more the H₂ content in the cathodic gas product with a subsequent reduction in the

output of the hydrocarbon species. However, it is necessary to keep CO_2 concentration in the gas feed composition at moderate levels (as will be clarified later) in some of the molten salts such as molten carbonates and chlorides, even for the sake of H_2 production.

6.3.1 Molten carbonate

In the case of the 425 °C run, the H_2 production rate in the run where $\text{CO}_2/\text{H}_2\text{O}=9.2$, was more than ten times the rate obtained when $\text{CO}_2/\text{H}_2\text{O}=15.6$ (Table 6.6). Indeed, H_2O vapour content in the gas feed was not enlarged in the second run in Table 6.6 but CO_2 content itself was reduced instead by diluting the feed gas with Ar. However, hydrocarbon fuel formation rather than CH_4 in general was rare in the second run obviously because of the high rate of H_2O reduction to H_2 and lower feasibility of hydrocarbon formation. CH_4 was the predominant hydrocarbon fuel though in this case. Moreover, it can be noted that the CO content was reduced by 45% in the second run supporting the last conclusion (hydrocarbon formation from the Fischer-Tropsch reaction). The partial oxidation of CH_4 though could be rare also in the media with a high content of H_2O vapour due to the lack of O^{2-} ions as the latter can be consumed, releasing OH^- in the salt according to reaction 2.51.

It was confirmed in many molten salt applications that the OH^- ion is the ion most responsible for hydrogen gas production from H_2O vapour introduced to molten salt (White and Twardoch 1983), incurring relatively higher current density than the case of lower H_2O content (or higher $\text{CO}_2/\text{H}_2\text{O}$ ratio) (Figure 6.19). The generation of hydrogen in that case ($\text{CO}_2/\text{H}_2\text{O} = 9.2$) is rapid and thus the residence time for hydrocarbon formation will be lower.

On the other hand, in addition to the intense aggregated current efficiency of the total product (up to 100%) in both cases, the calorific heat (heating values)

of the products obtained in the second run can offer (or compensate) 45% of the energy consumed during electrolysis thanks to the high production rate of H_2 .

In the case of the 500 °C run though, it can be noticed clearly that the increased H_2O content in the gas feed does not lead to higher H_2 production rates as the last case for 425 °C (Frangini and Masi In press) (from fast or rapid H_2O reduction). H_2 rates did not increase by higher levels possibly because of lower H_2O solubility (as will be illustrated later), reducing HCO_3^- ions produced for H_2O reduction to H_2 (reactions 2.55 and 2.56).

Therefore, H_2 production was still feasible by increasing the temperature but unfortunately this feasibility during the second run (at 500 °C), was not found to have resulted in higher production rates for various hydrocarbon species due to the lower residence time available for conversion at the cathode surface (if the hydrocarbon formation has been indeed confirmed from the Fischer Tropsch process).

On the other hand, the presence of CO_2 at an adequate content in the feed gas is important besides H_2O vapour for the production of H_2 in addition to CO and hydrocarbons at 1.5 V. Moreover, it was found that the solubility of CO_2 increases in the molten carbonates by increasing the temperature through which H_2O solubility can be decreased in turn. Thus reaction 2.51 will be infeasible and O^{2-} ions should still be available at this time. The partial oxidation of methane therefore can occur even at a CO_2/H_2O ratio of 9.2.

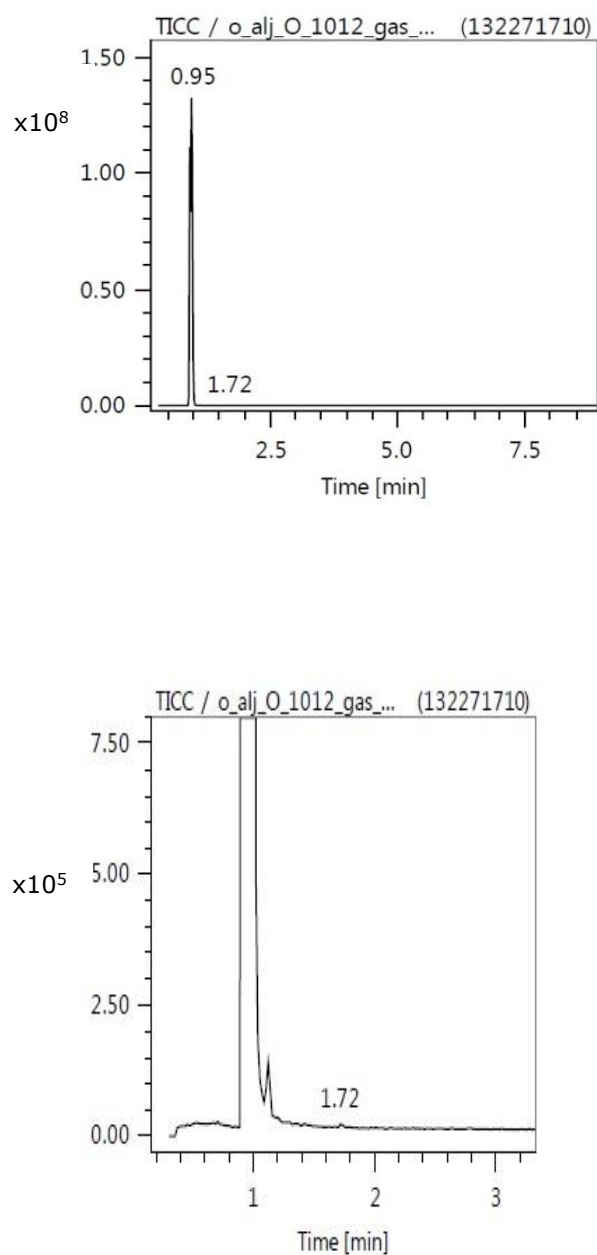


Figure 6.13. Total ion current (on the top and its expansion on the bottom) of the gases eluting from GC before fragmentation in mass spectrometry after injection from the gas sample taken during electrolysis of the molten carbonates at 1.5 V and 500°C. A peak of gases eluting at 1.72 minute retention time apart from the standard background peak, is also noted.

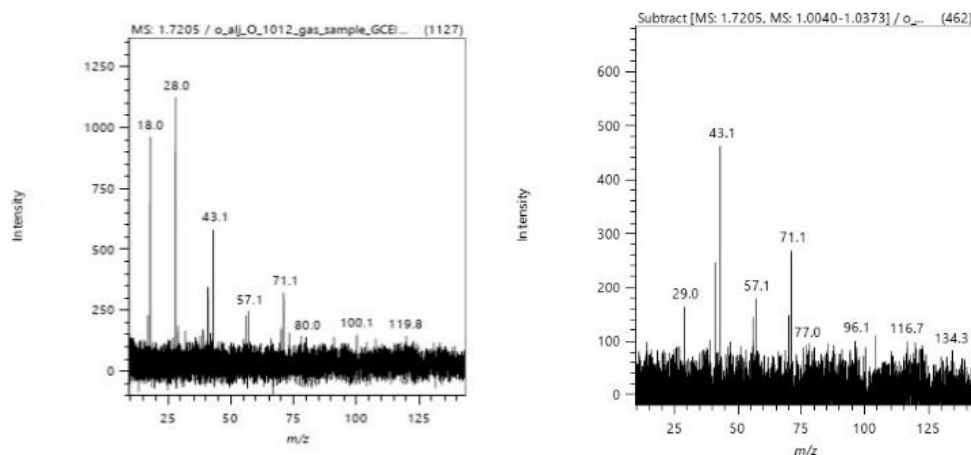


Figure 6.14. Left: Mass spectrum of gases eluting at 1.72 minute retention time as shown in Figure 6.1, Right: the same mass spectrum analysis (as left) after subtracting the background permanent gases eluting from the GC at the same time with a hydrocarbon product.

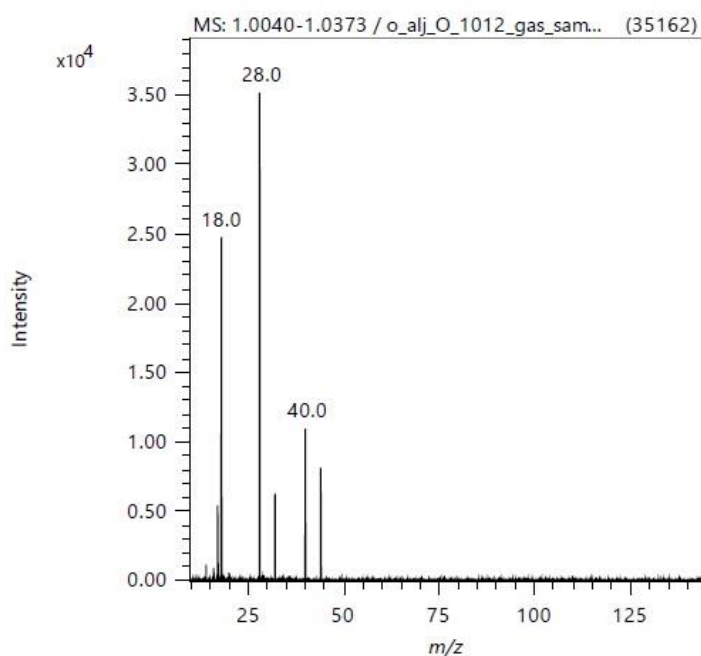


Figure 6.15. Mass spectrum of gases eluting between 1-1.04 minute retention time as shown in Figure 6.1, to see the kind of gases in a permanent gas product eluting before the hydrocarbon gas.

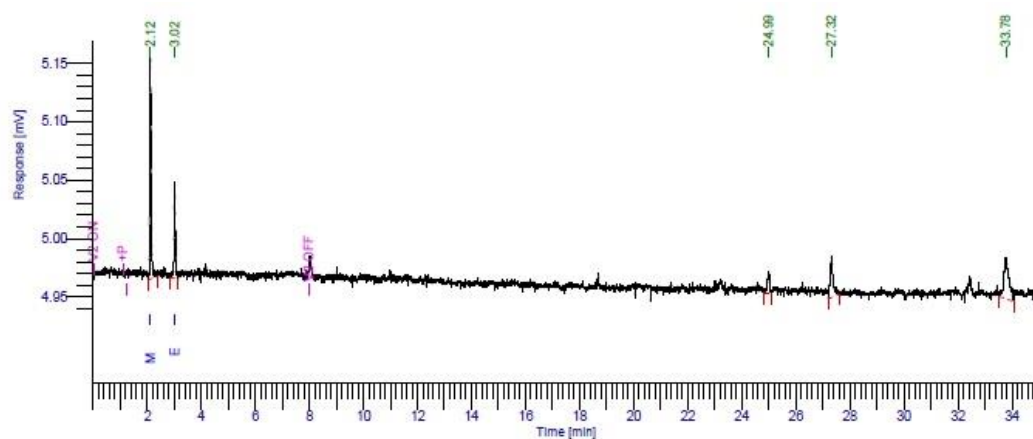


Figure 6.16. FID detector analysis of the cathodic gas sample taken during electrolysis at 1.5 V and 500 °C as obtained from Elmer GC (run 1).

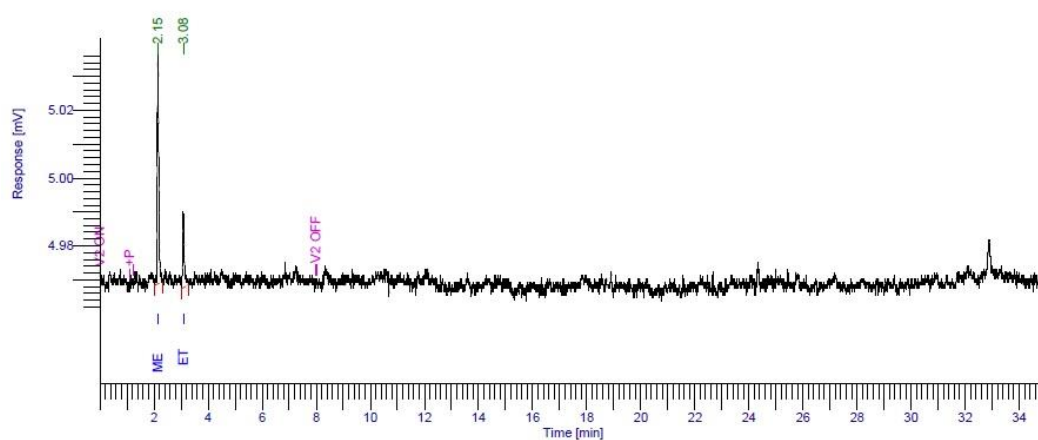


Figure 6.17. FID detector analysis of the cathodic gas sample taken during electrolysis at 1.5 V and 500 °C as obtained from Elmer GC (run 2).

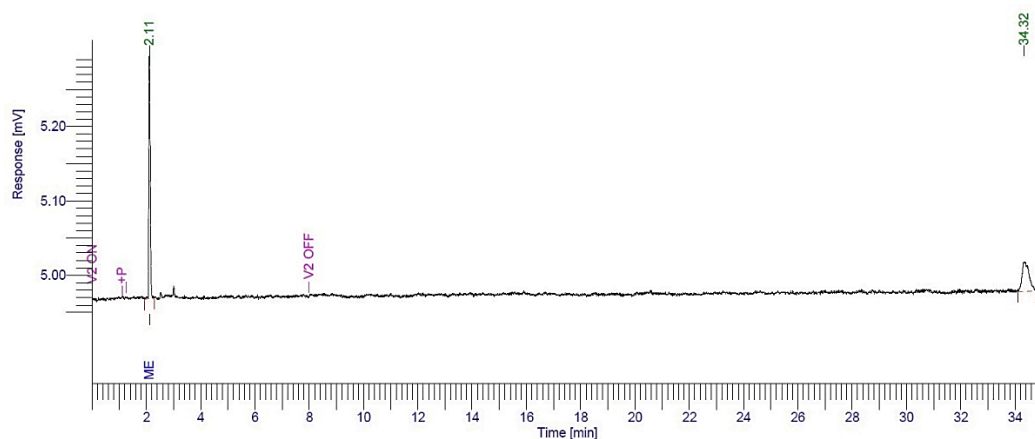


Figure 6.18. FID detector analysis of the cathodic gas sample taken during electrolysis at 1.5 V and 500 °C as obtained from Elmer GC (run3).

Table 6.6. Specification of the cathodic gas product during electrolysis in the molten carbonates under 1.5V cell voltage at 425 °C and different gas feed composition specified by CO₂/H₂O ratios using GC analysis (H₂, CO₂ and CO from the TCD channel whereas CH₄ and C₂-C₅ products from the FID channel

Run	CO ₂ /H ₂ O	Product	Gas product composition (Vol.%)	Uncertainty of gas composition	Production rate (μmol. cm ⁻² . h ⁻¹)	Current efficiency (%)	Heating value (J)	Energy consumption (J)
1	15.6	H ₂	0.217	± 0.04	4.4	11.9	11.4	114.2
		CH ₄	0.056	± 0.005	1.1	12.5	10.4	
		C ₂ =-C ₄ =	0.091	± (0.002-0.005)	1.8	43	37.5	
		CO	0.58	± 0.09	11.7	31.8	35.3	
		CO ₂	52.7	----	----	----	----	
2	9.2	H ₂	2.34	± 0.08	95.05	73	70.8	204
		CH ₄	0.1	± 0.01	4	12.1	9.6	
		CO	0.32	± 0.03	13	10	11.3	
		CO ₂	38.3	----	---	---		

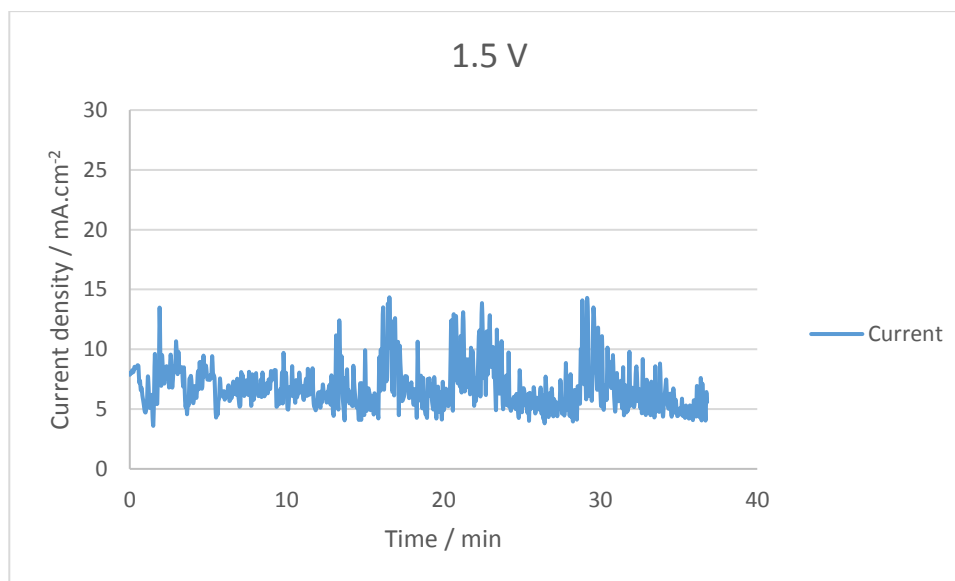


Figure 6.19. Current-time curves resulting from electrolysis performed in molten carbonates at 1.5 V, 425 °C and a CO₂/H₂O ratio of 9.2.

CH₄ was already confirmed from the first peak at approximately 2 min retention time during FID analysis from GC (Figures 6.16-6.18). For C₂H₄, the peak was confirmed at around 3 min for the same analysis (Figures 6.16-6.18) from gas samples of the standard mixture and several experiments (Table 3.4).

CO and C₂H₄ could not be confirmed clearly from the MS analysis as they are all mixed with the permanent gas in the first peak of the total ion current analysis (Figure 6.13). Actually, the species of permanent and atmospheric gases (CO, CO₂, Ar, N₂, O₂, H₂O except H₂) can be found even in any peak during the analysis of the total ion current. However, peak 28 in the mass spectrum (Figure 6.15) can be proved for CO or C₂H₄ and not just for N₂ (from contaminated air) as the ratio of the intensities between peaks 28 and 32 (for O₂) does not correspond to the molar ratio of N₂/O₂ in the normal environment

of air (80/20). Therefore, peak 14 can be shown as a tiny peak for the loss of fragment CH_2 from C_2H_4 molecules and another small peak of 16 for loss of O from CO molecules. Peaks 18, 40 and 44 subsequently stand for H_2O , Ar and CO_2 molecules respectively.

By matching Figure 6.14 of the mass spectrum of the gas molecule (C_7H_{10} or more) eluting at 1.72 minute (despite the noise of small peaks) with Figure 6.1 of the spectrum for C_8H_{18} standard elution at approximately 2.9 minute in a different analysis at the same temperature programme (method), it can be seen that the gas follows the same behaviour as the standard in Figure 6.1 and can be identified as C_7H_{16} for the following reasons:

1. There is no prominent peak of an even number to show the spectrum of the total ion resulting from the hydrocarbon molecule except 100 (for C_7H_{16}) as the peak was clarified for C_8H_{18} as 114 in Figure 6.1, thus holding a lower intensity than its fragments (85, 71, 57 and 43). Basically, the last fragments were shown in the spectrum due to the loss of 14 (CH_2) from fragmentation of the molecule C_8H_{18} during the analysis.
2. The adjacent fragments from C_8H_{18} (99 for C_7H_{15}) and C_7H_{16} (85 for C_6H_{13}) were not shown in both Figures because of the loss of peak 29 (for CH_3CH_2) already from both molecules.
3. The fragments lower than the adjacent ones (85 in Figure 6.1 and 71 in Figure 6.14) were shown in higher intensities than the other fragments except 43 in both Figures.

Table 6.7. Specification of the cathodic gas product during electrolysis in the molten carbonates under a 1.5 V cell voltage at 500 °C and different gas feed composition specified by CO₂/H₂O ratios using GC analysis (H₂ and CO from TCD channel and CH₄ from FID channel) and mass spectrometric analysis (for C₆H₁₄ and C₇H₁₆).

Run	CO ₂ /H ₂ O	Product	Gas product composition (Vol.%)	Uncertainty of gas composition	Production rate (μmol. cm ⁻² . h ⁻¹)	Selectivity (%)	Current efficiency (%)	Heating value (J)	Energy consumption (J)
1	15.6	H ₂	0.2	± 0.04	4	--	5.1	7.3	171
		CH ₄	0.02	± 0.006	0.4	7	2	2.6	
		C ₆ H ₁₄	0.12	± 0.01	2.4	42.1	58	75	
		C ₇ H ₁₆	0.06	± 0.003	1.2	21	32.4	43.3	
		CO	0.1	± 0.01	1.7	---	2.2	3.7	
2	9.2	H ₂	1.05	± 0.05	74.2	---	28.7	72	297
		CH ₄	0.06	± 0.005	5	3.5	8.2	18.6	
		C ₂ H ₄	0.016	± 0.002	1.2	0.8	2.9	7.1	
		C ₇ H ₁₆	0.017	± 0.002	1.5	1	13	29	
		CO	0.88	± 0.04	68	---	26.3	76.5	

Moreover, it can be noted that the intensity of the peaks of fragments in the case of the CO₂/H₂O ratio of 15.6 is higher than that for the case of the CO₂/H₂O ratio equal to 9.2 in the previous section.

The formation of larger hydrocarbon species (over C₆H₁₄) can be justified due to dense carbon deposition or high CO adsorption at the cathode because of the high partial pressure of CO₂ (as stated before), particularly in the case when CO₂/H₂O=15.6 as confirmed in the investigation of dry CO₂ reduction (Ijije, Sun et al. 2014). Also, the reduction of CO₂ to CO or C can occur at less reductive potentials than the case for the lower partial pressures of CO₂ in the feed gas (Chery, Lair et al. 2015).

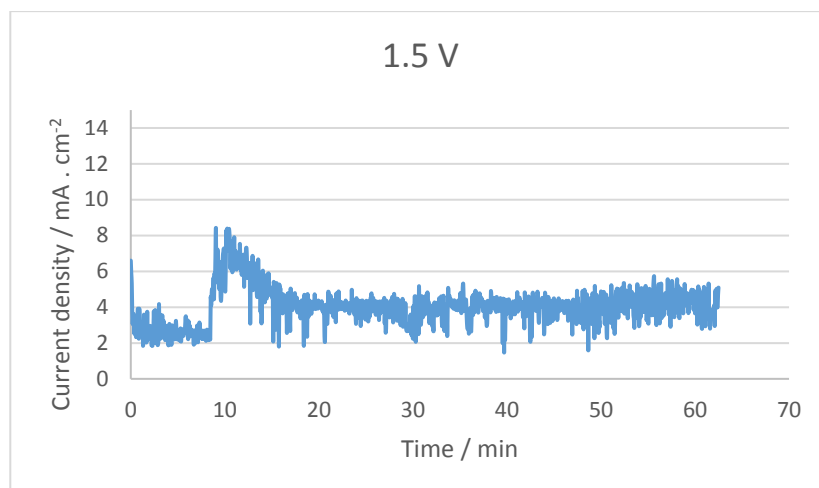


Figure 6.20. Current-time curves resulting from electrolysis performed in molten carbonates at 1.5 V, 500 °C and a CO₂/H₂O ratio of 15.6.

On the other hand, employing a humid feed gas with the composition of undiluted CO₂ at CO₂/H₂O=9 for instance will not contribute to significant results, particularly in the run at 500 °C where the CO₂ composition was 90% of the feed gas as shown in Table 6.8. In addition to the difficulty of obtaining a proper gas product during electrolysis at this stage (due to the high solubility of CO₂), H₂ and CO were the predominant products without any advantages observed in terms of the quantity of the obtained hydrocarbons.

Also in contrast, the use of highly diluted CO₂ with H₂O by a CO₂/H₂O ratio between 1 and 6, was inapplicable as the amount of CO₂ could not be enough even for the formation of H₂ (reaction 2.55-56) in addition to CO or carbon deposition in addition on the cathode.

Table 6.8: Production rates of the cathodic gas product during electrolysis in the molten carbonates under a 1.5V cell voltage at 500 °C and different gas feed composition specified by CO₂/H₂O ratios and volume percent of CO₂.

Run	CO ₂ % in feed gas	CO ₂ /H ₂ O	Production rates μmol. h ⁻¹ . cm ⁻²			
			H ₂	CH ₄	C ₆ +C ₇	CO
1	32	9.2	74.2	5	1.5	68
2	48.4	15.6	4	0.4	4.1	1.7
3	90	9	2	0.04	0	0.1

6.3.2 Molten hydroxide

In spite of the high reactivity of CO₂ with the molten hydroxide, this gas itself could be reduced directly during electrolysis to produce CO or hydrocarbon fuels. The presence of large amounts of H₂O in the feed gas composition can be a solution to avoid carbonate ion formation by driving the reaction (2.83) in the opposite direction.

However, the introduction of a higher content of H₂O in the gas feed due to a CO₂/H₂O ratio of 1, will unfortunately lead to a higher H₂ content than hydrocarbons or CO in the cathodic gas product.

Therefore, the employment of moderate H₂O compositions in the feed gas such as a CO₂/H₂O of 5.6 in the experiment of electrolysis of LiOH-NaOH (27-73% Mol) at 2 V and 275 °C, can lead to the production of the cathodic gas product with less H₂ and higher CH₄ than the gas product from electrolysis at the same conditions and a CO₂/H₂O ratio of 1 as shown in Table 6.9.

Although carbonate ions can be formed in both cases, the following points were observed about the gas product:

1. CO was produced exclusively in the second run as it was absent in the first run. This result can confirm the effect of CO₂ on electrolysis in the molten hydroxide despite the rapid reaction of CO₂ with the salt.
2. The H₂ production rate reduced by 85% compared to the first run.
3. The CH₄ production rate increased more than seven times the rate obtained during the first run.

It was observed that retaining water vapour in the feed gas composition by the above CO₂/H₂O ratio of 5.6 is important to achieve reasonable amounts of H₂, CO and hydrocarbons during electrolysis.

Therefore, performing electrolysis at moderate CO₂/H₂O ratios between 5 and 6 will contribute to reasonable production rates of CH₄, at least with lower H₂ and CO production rates.

Table 6.9: Specification of the cathodic gas product during electrolysis in the molten hydroxides under 2V cell voltage at 275 °C and a different gas feed composition specified by CO₂/H₂O ratios using GC analysis (H₂, CO₂ and CO from TCD channel and CH₄ from FID channel) and mass spectrometric analysis (for C₆H₁₄ and C₇H₁₆).

Run	Molten salt	CO ₂ /H ₂ O	Product	Composition percentage in product (Vol.%)	Uncertainty of gas composition	Moles *10 ³	Production rate (mmol.h ⁻¹)	Current efficiency (%)
1	LiOH-NaOH (27-73) Mol%	1	H ₂	34.1	± 0.9	3.5	14	99.5
			CH ₄	0.02	± 0.006	0.002	0.01	0.05
			CO	0	0	0	0	0
			CO ₂	0.46	---	0.05	---	----
2	LiOH-NaOH (27-73) Mol%	5.6	H ₂	4.44	± 0.1	0.455	0.91	13
			CH ₄	0.15	± 0.01	0.017	0.034	2
			CO	0.39	± 0.03	0.04	0.08	1.1
			CO ₂	0.75	----	0.08	----	----

6.4 Summary

In this chapter, the study of process variables of temperature, applied cell voltage and CO₂/H₂O ratio was carried out in molten carbonates and hydroxides to investigate improvements for fuel production.

As for the electrolytic temperature effect in molten carbonates, it was found that new hydrocarbon had been obtained as the temperature increased from 425 °C to 500 °C due to the persistent reduction of H₂O to H₂. Various new hydrocarbon species with a molecular weight larger than C₅ were found in the product after electrolysis at 500 °C by MS analysis. Despite the high observed values, this behaviour regarding the H₂ production rates was found even in the

molten hydroxide case when the electrolytic temperature was increased from 220 °C to 275 °C with unchanged flowrates of CO and CH₄ rates. The production rates and current efficiencies of H₂, CO and CH₄ declined though to very low values at a higher electrolysis temperature of 335 °C.

For the applied cell voltage effect, it was confirmed that electrolysis and hydrocarbon formation in molten carbonates were both more feasible at 1.5 V than at 2 V due to prospective carbon formation. In the molten hydroxide case though, CH₄ production rates increased dramatically when the applied voltage was increased from 2 to 3 V despite the reduced current efficiencies.

For the CO₂/H₂O ratio of the inlet gas effect, CH₄ was the predominant hydrocarbon product in the case of lower CO₂/H₂O ratios with a high rate of H₂ formation at 425 °C in molten carbonates. However, despite the low production rates, some hydrocarbon products with higher molecular weights can be generated when electrolysis is applied at higher ratios of CO₂/H₂O in the feed gas and at 500°C. For the molten hydroxide case though, the ratio should be kept as 5.6 to achieve the appropriate production rates of H₂, CO and CH₄.

Chapter 7

Optimisation of Hydrocarbon Production and Process Variables

In this chapter, the study of the optimised design of the reactor and process variables for a higher hydrocarbon production rate and efficiency, will be conducted. In the beginning, the reactor has mimicked the configuration of the previous electrolyser performed for carbon deposition. The major difference was the presence of ceramic tubes that were inserted inside the reactor to surround the cathode and anode rods and collect the product gases. The process of hydrocarbon formation or generally fuel production was confirmed directly or indirectly during the electrolysis of CO_2 and H_2O in the various mediums containing molten salts. The production rates of CO , H_2 and hydrocarbon gases in general were set as a basis in this chapter to compare the different reactor designs and process variables. This chapter is divided into two sections as seen from the title; optimisation of the best reactor design employed and the optimum process variables for fuel production. The optimisation was performed focusing on the molten carbonate salt due to the high efficiency of hydrocarbon fuels in particular.

7.1 Hydrocarbon content

Some hydrocarbon species were discovered in the previous chapters besides hydrogen and CO fuels, particularly in the ternary molten carbonates at 1.5 V. The production rates were calculated employing different temperatures and

CO₂/H₂O ratios. In this chapter, the values of product concentrations were gathered to determine the optimum conditions for hydrocarbon fuel production and to figure out the ranking of the hydrocarbon species based on the molecular weight due to these conditions. Basically, product concentration was calculated as a percentage of the production rate of the particular cathodic fuel in $\mu\text{mol}/\text{cm}^2\cdot\text{h}$ to the total rate of the products. Figures 7.1 and 7.2 were plotted to display the product concentrations of H₂, CO and hydrocarbons (HC) with the combined current efficiencies (of total products) at two different temperatures (425 and 500 °C) under the CO₂/H₂O molar ratios (15.6 and 9.2) of the feed gas.

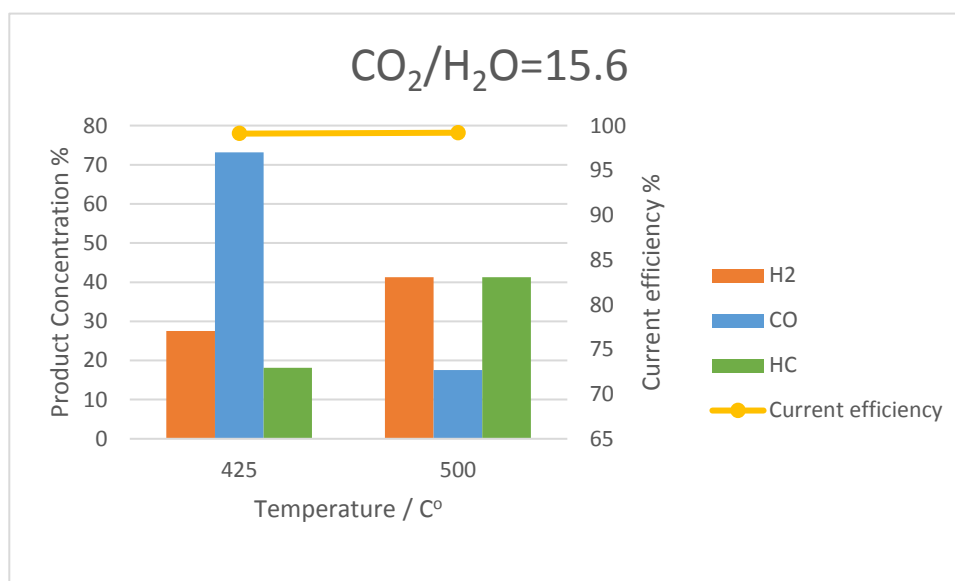


Figure 7.1: A column chart of the production rates of CO, H₂ and hydrocarbon species in general; in addition to current efficiency obtained employing electrolysis in the ternary molten carbonates at 1.5 V and two different temperatures at a 15.6 value of CO₂/H₂O molar ratio for the feed gas.

First of all, it can be confirmed that CO and H₂ have been generally produced in molten carbonates by the co-electrolysis of CO₂ and H₂O at low temperatures (<500 °C) with high current efficiencies, whereas CO (in particular) is conventionally produced or synthesised under higher temperatures (>800 °C) (Wu, Liu et al. 2017). The generation of H₂ was performed by the reduction of H₂O in molten carbonates even without the addition of hydroxide salt (such as NaOH).

It can be seen from Figure 7.1 that the highest CO concentration is achieved in the electrolysis at 425 °C under a CO₂/H₂O ratio of 15.6. The hydrocarbon species were found in this case in the range C₁-C₄ with the priority for olefin compounds as illustrated in previous chapters. Therefore, it can be concluded at this stage that light hydrocarbon (<C₅) products, particularly CH₄, can be formulated using electrolysis at a low temperature condition (425 °C) (Figures 7.3 and 7.4). Also, the ratio of CO/H₂ production rates can be controlled by the molar ratio of CO₂/H₂O in the feed gas to conduct electrolysis at 425 °C. However, apart from the case of a run at 425 °C under a CO₂/H₂O ratio of 15.6, there was a preferential tendency for H₂ generation during electrolysis; particularly in the case of a higher H₂O content of the feed gas (CO₂/H₂O ratio of 9.2) or when the hydroxide mixture with a carbonate salt electrolyte (such as Li_{0.85}Na_{0.61}K_{0.54}CO₃-2LiOH) was used as confirmed in recent literature (Wu, Ji et al. 2016). The predominance of CH₄ production was very clear among other hydrocarbon species in this case (Figure 7.4).

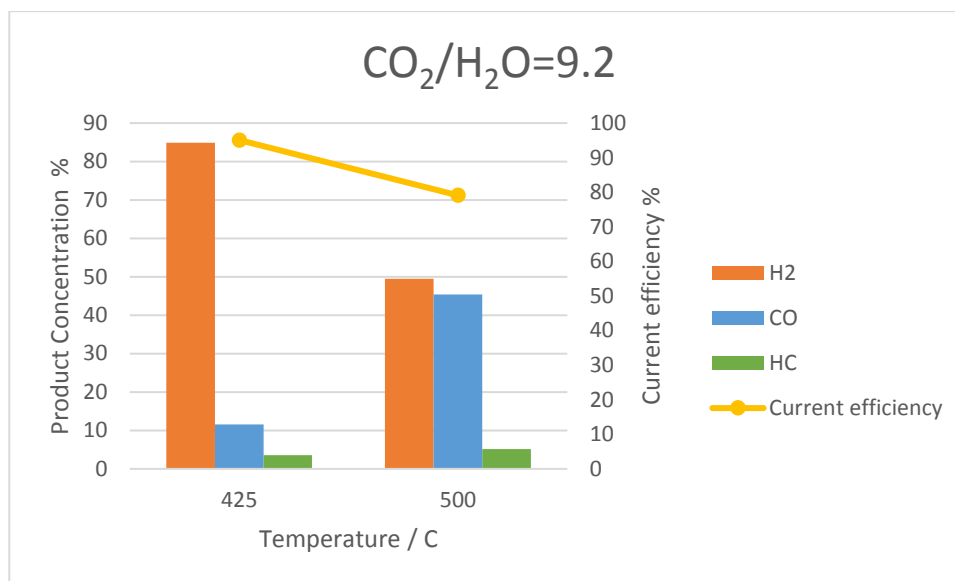


Figure 7.2: A column chart of the production rates of CO, H₂ and hydrocarbon species in general in addition to the current efficiency obtained employing electrolysis in the ternary molten carbonates at 1.5 V and two different temperatures under a 9.2 value of the CO₂/H₂O molar ratio of the feed gas.

Furthermore, it was confirmed that the existence of H₂ in an appropriate amount on the cathode in the molten carbonates, can prevent the formation of solid carbon as an undesired product at low temperatures (<500 °C). This can also reduce the production rate of hydrocarbons on the other hand. Therefore, there is a clear relationship between the production rate of H₂ and the formation of hydrocarbons at this stage.

It can also be noticed that there is a tangible increase in hydrocarbon production at increasing temperatures, particularly under a CO₂/H₂O ratio of 15.6 at 500 °C (Figures 7.1 and 7.2). In this case, the hydrocarbon concentration in total can reach the optimum value of 41% of the total products, essentially the same value as for H₂ production.

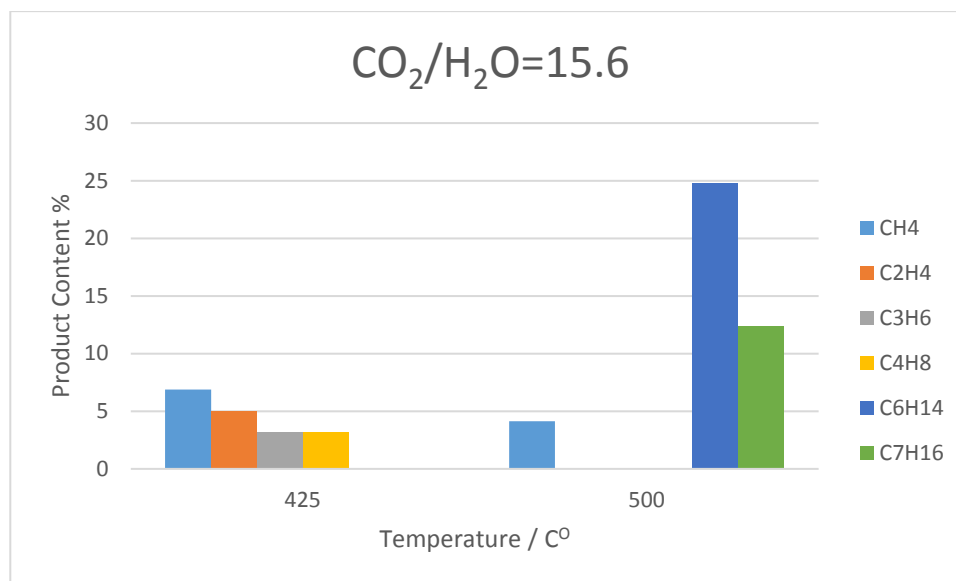


Figure 7.3: A column chart of the production rates of the specific hydrocarbon species obtained employing electrolysis in the ternary molten carbonates at 1.5 V and two different temperatures under a 15.6 value of the $\text{CO}_2/\text{H}_2\text{O}$ molar ratio for the feed gas.

The hydrocarbon species generated during electrolysis at 500 °C included C_6H_{14} and C_7H_{16} in the case of a higher CO_2 content of feed gas ($\text{CO}_2/\text{H}_2\text{O}$ of 15.6) as confirmed by the GC-mass spectrometric analysis. C_7H_{16} was also found in the case of a lower CO_2 content suggesting that high molecular weight hydrocarbon species can be produced at high temperature levels (>425 °C) where appropriate amounts of H_2 and CO are still available for hydrocarbon formation.

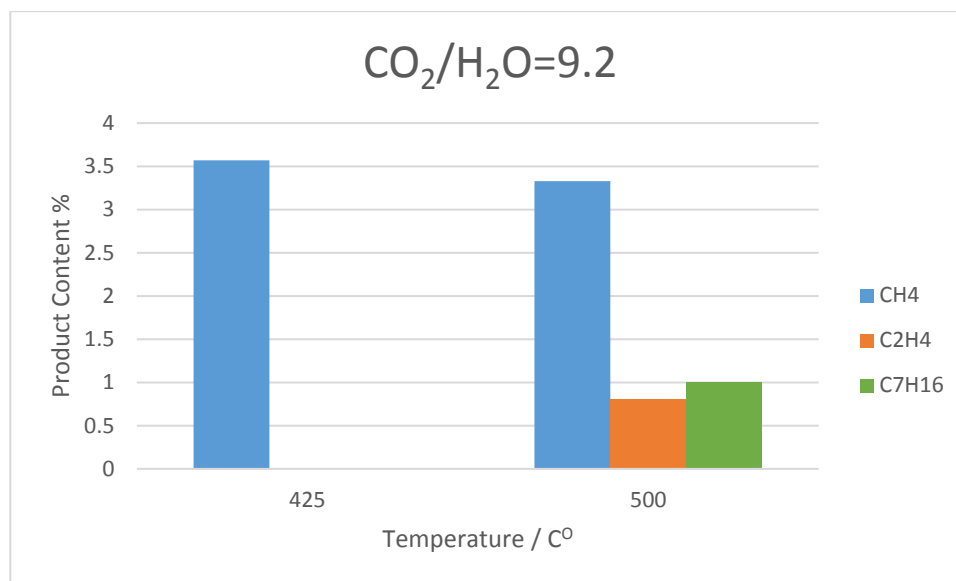


Figure 7.4: A column chart of the production rates of the specific hydrocarbon species obtained employing electrolysis in the ternary molten carbonates at 1.5 V and at two different temperatures under a 9.2 value for the $\text{CO}_2/\text{H}_2\text{O}$ molar ratio of the feed gas.

7.2 Current efficiency

Generally the formation of hydrocarbon species increases the combined current efficiency of cathodic products as illustrated in the previous chapters. It can be noticed from Figure 7.1 that the current efficiency does not change and is maintained at the high level of $\sim 99\%$ (despite a significant rise in current density) when the temperature was increased from 425 to 500 °C under a molar ratio of $\text{CO}_2/\text{H}_2\text{O}$ of 15.6. This action can be imputed to increasing hydrocarbon formation in general and the evolution of new and long-chain (high molecular weight) hydrocarbon species at high temperatures as illustrated in the previous section (Figure 7.5). Therefore, the combined current

efficiency of hydrocarbon products increased from 55% to 92% at this stage in contrast with the efficiencies of H_2 and CO which remained reduced.

However, the total current efficiency of the entire cathodic product reduced clearly from 95% to 79% by increasing the temperature under a CO_2/H_2O ratio of 9.2 due to the reduction of hydrocarbon generation in this case, despite the formation of C_7H_{16} (Figure 7.2). Alternately, the combined current efficiency of the hydrocarbon species (due to C_7H_{16} formation), increased from 12% at 425 °C to 24% at 500 °C (Figure 7.6).

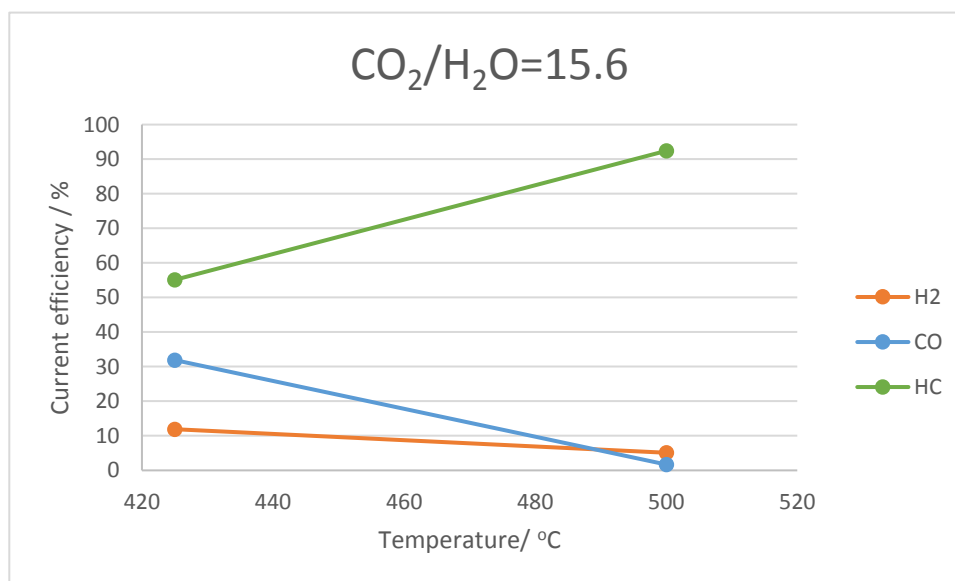


Figure 7.5: The plotted current efficiencies of CO, H₂ and hydrocarbon species in general versus temperature for electrolysis of the ternary molten carbonates at 1.5 V under a 15.6 value for the CO_2/H_2O molar ratio of the feed gas.

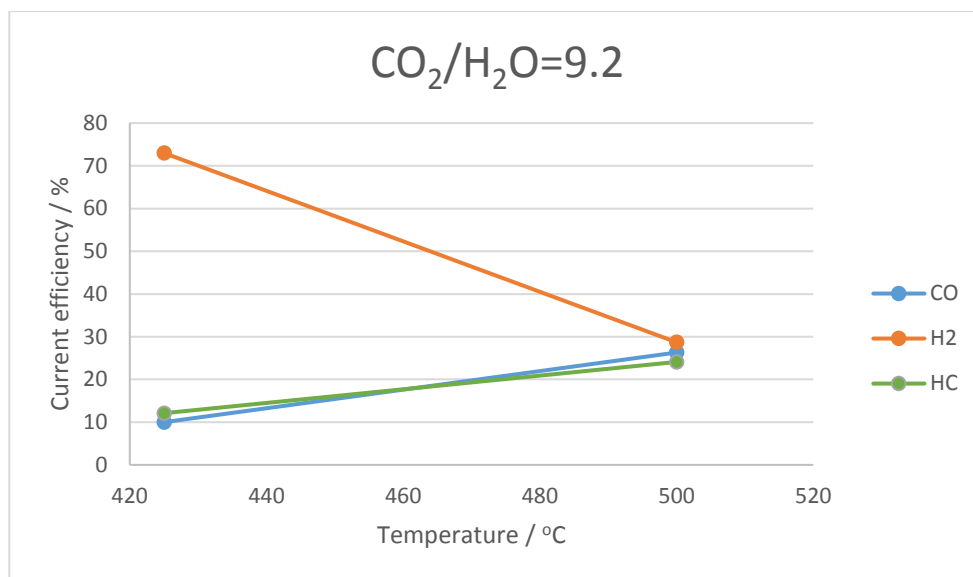


Figure 7.6: The plot current efficiencies of CO, H₂ and hydrocarbon species in general versus temperature for electrolysis of the ternary molten carbonates at 1.5 V under a 9.2 value for the CO₂/H₂O molar ratio of the feed gas.

Subsequently, the plots of current efficiencies with temperatures in separate figures (7.5 and 7.6), offer another proof for confirming the optimum conditions for hydrocarbon formation at 500 °C under a molar ratio of CO₂/H₂O of 15.6. It is worth mentioning that the high yield of hydrocarbon formation was found also from the reaction of atomic H with adsorbed carbon at 500 °C in the tungsten effusion tube shown in Chapter 2 (Snelson 1974).

7.3 Summary

In this chapter, the optimum conditions for hydrocarbon fuel production have been indicated based on the product content in the entire cathodic product and current efficiency during electrolysis in the molten carbonate salt electrolyte at

1.5 V. The optimisation was determined for results at two different temperatures: 425 and 500 °C, and two different conditions of the CO₂/H₂O molar ratio of the feed gas. Light hydrocarbons (up to C₅ species) were generated under the CO₂/H₂O ratio of the feed gas of 15.6 at a temperature of 425 °C with a high current efficiency. CH₄ production is predominant and very clear in the case of a high H₂O content of the feed gas (CO₂/H₂O of 9.2) in general. The best conditions for hydrocarbon formation were absolutely in the case of CO₂/H₂O=15.6 at 500 °C, where long-chain hydrocarbon products with high molecular weights (> C₅) were confirmed.

Chapter 8

Conclusions and Future works

8.1 Conclusions

1. The production of hydrocarbon gases from the electrolytic co-conversion of CO_2 and H_2O in molten salts, including hydroxides, has been investigated as an appropriate way for tackling the positive footprint of carbon emissions from power stations and other diverse industrial operations.
2. The electrolytic co-conversion of CO_2 and H_2O in molten salts to gaseous hydrocarbons can proceed at mild temperatures (200-600 °C) which are more desirable for hydrocarbon production in comparison with the high temperatures (800-900 °C) that are needed for solid oxide electrolysis as reported in the literature because re-oxidation of the gaseous hydrocarbons is more feasible at higher temperatures.
3. Molten salts though, as ionic liquids, can basically enable the co-reduction of CO_2 and H_2O to H_2 and CO (or carbon) at the applied temperatures (200-600 °C) before the prospective formation of hydrocarbon fuels at the same stage in the reactor.
4. The CH_4 gas was the only hydrocarbon detected in this work, in agreement the previously reported investigations of the electrolysis of the pure or unmixed molten carbonate salt. The present of this gas was justified due to the moisture associated with gas feed during the electrolysis of the molten carbonate, producing H_2 gas. It has also been found that hydroxide ions OH^- plays a significant role for hydrogen gas production from the steam introduced to molten salt.
5. In other investigations though, small amounts of hydrocarbons with higher molecular weight (up to C_5 products) were detected beside CH_4 in the

cathodic gas product from the direct electrolysis of various mixtures of molten hydroxides and carbonate salts between (450-500 °C). The electrolysis was performed without CO₂ or H₂O introduction. Alkene hydrocarbons were found during the electrolysis of the mixture of Li_{0.85}Na_{0.61}K_{0.54}/0.08LiOH at 450 °C, whereas alkane hydrocarbons were detected mainly in the experiment on the hydroxide-carbonate mixtures with higher hydroxide content, e.g. the Li_{0.85}Na_{0.61}K_{0.54}/2LiOH mixture at 500 °C.

6. The new molten salt electrolyser used in this work was designed according to one of the previously reported studies dedicated actually for CO₂ reduction to CO. The new electrolyser included ceramic tubes for collecting the cathodic and anodic gases, instead of the partitioned cell with both the cathode and anode compartments used in the previously reported design.
7. The new electrolyser was tested (for instance) using two different cathode materials in the ternary molten carbonates (Li₂CO₃-Na₂CO₃-K₂CO₃) at 500 °C. It has been found that the hydrocarbon species produced in the case of a titanium foil cathode were specifically higher in molecular weight with higher production rates than the products obtained using a mild steel rod cathode. Thus, the titanium foil is considered as the preferred cathode material for experiments in molten carbonates particularly.
8. Formation of alkenes was found more feasible than that of alkanes during the electrolysis of the ternary molten carbonate mixture (Li₂CO₃-Na₂CO₃-K₂CO₃, 43.5:31.5:25 mol%) at 425 °C when the feed gas was mixed CO₂ and H₂O in a molar ratio of 15.6. This outcome can be analogous with the hydrocarbon product obtained from the electrolysis of lean hydroxide and carbonate mixture at quite similar temperatures. The hydrocarbons could have formed according to the Fisher-Tropsh process due to the reaction of CO with H₂, both of which might have primarily adsorbed on the cathode.

Because of the relatively high temperature medium, current efficiencies for producing different hydrocarbon species were particularly higher in the molten carbonates than those in molten chlorides or hydroxides.

9. The CH₄ gas was the predominant hydrocarbon fuel produced during the electrolysis in pure molten hydroxide under mixed CO₂ and steam in general, and particularly at 275 °C.
10. In unmixed molten carbonates under CO₂/H₂O of 15.6 in molar ratio at 500 °C, long-chain hydrocarbon products with high molecular weight (> C₅) were detected.
11. The cathodic product can also include carbon as a dendritic or dense deposit at 500 °C or higher temperatures in molten carbonates. Such deposit carbon may justify the formation of higher molecular weight hydrocarbons up to C₇H₁₆ particularly when the CO₂/H₂O feed gas had a molar ratio of 15.6.
12. In molten carbonates, it was also found that the CO₂ gas should be used by 32% of the feed gas with the CO₂/H₂O molar ratio of 15.6 to achieve high production rates of hydrocarbons in general. Higher concentrations of CO₂ would reduce the general production rates due to the contamination of CO₂ in the product gas. Lower concentrations of CO₂ in the feed gas though will require higher cell voltages to achieve the same result, but at the expenses of the current efficiencies of products.

8.2 Future work

1. The project experienced some practical difficulties in terms of access the experimental equipment and accordingly there were some simplifications in the experimental procedures. Some arrangements should be done on:
 - a. Temperature monitoring in the reactor during the electrolysis by fitting an immutable thermocouple in the retort.

- b. Analysing anodic gas product beside the cathodic one (by GC) to know the accurate amounts of the entire products from electrolysis in addition to the unreacted CO_2 and help perform the mass balance calculations for instance.
 - c. Applying a PTFE or an alumina insulation material to cover the unsubmerged rods (cathode & anode) above the molten salt to determine the working surface area of the electrode more accurately inside the molten salt.
 - d. Arranging another gas sampling for mass spectrum analysis beside the sample of normal GC at the same time during electrolysis to conform the data from both analyses.
2. Due to the unavoidable presence of CO_2 in the product especially in molten carbonates, two or multiple electrolyzers should be arranged in series to absorb the remaining amounts of CO_2 associated with the products and therefore increase the contents and production rates of product fuels.
3. The reactor can be rearranged to use the previously reported partitioned cell, instead of the existing electrolyser with ceramic tubes. Thus, the previously reported design of the lithium carbonate electrolyser to reduce CO_2 to CO can be reproduced for the co-reduction of CO_2 and H_2O to hydrocarbons. The partitioned cell design would offer the opportunity to use the large surface area of molten salt inside both the cathode and anode compartments, sufficient to absorb the unreacted CO_2 and increase the production rate in general.
4. The co-electrolysis of CO_2 and H_2O could be done in molten carbonates at $500\text{ }^\circ\text{C}$, employing applied voltages, e.g. 2 or 2.5 V rather than 1.5 V as carbon deposition at this stage is not quick enough to generate the various hydrocarbon species feasibly.

5. The study of process variables including temperature, applied voltage and ratio of $\text{CO}_2/\text{H}_2\text{O}$ in the inlet gas should be performed for molten chlorides beside molten carbonates and hydroxides.
6. Various compositions of molten carbonates mixed with hydroxides salt can be employed to perform the electrolysis under the same conditions without CO_2 or H_2O introduction to compare the results with the outcomes from the recent investigations.

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