

Sustainable conversion of carbon dioxide into diverse hydrocarbon fuels via molten salt electrolysis

Ossama Al-Juboori, Farooq Sher, Saba Rahman, Tahir Rasheed,
and George Z. Chen



**University of
Nottingham**
UK | CHINA | MALAYSIA

University of Nottingham Ningbo China, 199 Taikang East Road, Ningbo, 315100, Zhejiang, China.

First published 2020

This work is made available under the terms of the Creative Commons Attribution 4.0 International License:

<http://creativecommons.org/licenses/by/4.0>

The work is licenced to the University of Nottingham Ningbo China under the Global University Publication Licence:

<https://www.nottingham.edu.cn/en/library/documents/research/global-university-publications-licence-2.0.pdf>



**University of
Nottingham**

UK | CHINA | MALAYSIA

Sustainable conversion of carbon dioxide into diverse hydrocarbon fuels via molten salt electrolysis

Ossama Al-Juboori¹, Farooq Sher^{2,*}, Saba Rahman³, Tahir Rasheed⁴, George Z. Chen^{1,5*}

¹*Department of Chemical and Environmental Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK*

²*School of Mechanical, Aerospace and Automotive Engineering, Faculty of Engineering, Environment and Computing, Coventry University, Coventry CV1 5FB, UK*

³*Department of Chemical Engineering, Aligarh Muslim University, Aligarh, UP 202002, India*

⁴*School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

⁵*Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Ningbo China, University Park, Ningbo 315100, China*

*Corresponding authors:

E-mail address: Farooq.Sher@coventry.ac.uk (F.Sher), George.Chen@nottingham.ac.uk (G. Chen)

Abstract

In recent decades, the unlimited use of fossil fuels mostly for power generation has emitted a huge amount of carbon dioxide in the atmosphere which in return has led to global warming. Here we use green technology, the molten salt electrochemical system comprising of titanium and mild steel as a cathode with graphite anode whereas molten carbonate ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$; 43.5:31.5:25 mol%), hydroxide (LiOH-NaOH ; 27; 73 and KOH-NaOH ; 50:50 mol %) and chlorides (KCl-LiCl ; 41-59 mol%) salts as electrolytes. This study investigates the effect of temperature, feed gas ratio $\text{CO}_2/\text{H}_2\text{O}$ and use of different cathode materials on hydrocarbon product along with current efficiencies. Gas chromatography and mass spectroscopy have been applied to

analyze the gas products. According to GC results, **more specific results in terms of high molecular weight and long chain hydrocarbons were obtained by using titanium cathodic material rather than mild steel.** The results revealed that among all the electrolytes, molten carbonates at 1.5V and 425°C produced higher hydrocarbons as C₇H₁₆ while all other produced CH₄. **The optimum conditions for hydrocarbon formation and higher current efficiencies in case of molten carbonates were found to be 500°C** under a molar ratio of CO₂/H₂O of 15.6. However, the current efficiencies do not change on increasing the temperature from 425 to 500°C and is maintained at 99% under a molar ratio of CO₂/H₂O of 15.6. The total current efficiency of the entire cathodic product reduced clearly from 95 to 79% by increasing the temperature under a CO₂/H₂O ratio of 9.2 due to the reduction of hydrocarbon generation in this case, despite the formation of C₇H₁₆. Therefore, due to its fast electrolytic conversion rate and low cost (no use of catalyst) the practice of molten salts could be an encouraging and promising technology for future investigation for hydrocarbon fuel formation.

Keywords: Renewable energy; CO₂ utilisation; electrochemical conversion; Molten salts electrolysis; Hydrocarbon **fuels and CO₂/H₂O.**

1 Introduction

With the increasing population, the demand for the energy resources (fossil fuels) have been increased drastically which in turn has resulted in the higher concentration of CO₂ in the atmosphere. Despite the fact that fossil fuels supply almost 80% of earth's energy, they have exacted an enormous toll on the environment, including global warming, as well as on humans¹. **Air pollution due** to the burning of fossil fuels has surplus the fatality rate of cardiovascular, pulmonary and other various diseases ².**Therefore, the approach to minimize CO₂ emission by**

using renewable sources of energy including solar, wind, geothermal as well as nuclear have gained much attention in the last few years^{3,4}. However, these renewable resources do not include sequestration of CO₂ through their electricity generation. Alternatively, to store the energy in the form of hydrocarbon fuels (CH₄, C₂H₄, C₂H₆ and C₃H₈) CO₂ capture and conversion is a feasible approach. Different carbon capture techniques reported in the literature include cryogenic fractionation, membrane separation, physical adsorption and chemical adsorption, whereas the chemical absorption method is considered as one of the most applied techniques⁵. Aqueous electrolysis, solid oxide electrolysis, photo catalytic reduction, proton exchange membrane, thermochemical cycles and electrolysis using molten salts are the various types of CO₂ conversion techniques explored in recent years⁶⁻⁸.

..The electrolysis is considered an effective method for the production of hydrocarbon fuel from CO₂ and H₂O. The aqueous electrolysis at low temperatures (<100 °C) was employed by scientists⁹, whereas suitable catalyst to reduce energy consumption and increase product selectivity is necessary¹⁰. Besides the low solubility of CO₂ in the medium, slow kinetics, low productivity due to unseparated products limits its future use¹¹. The high-temperature electrolysis offers both thermodynamic as well as kinetic advantages. Solid oxide electrolysis cells (SOEC) and molten salt cells are used in high temperatures. SOEC produces syngas as well as hydrocarbons^{12,13} but the instability of Ni-based electrode, 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^{14,15}.

Different from SOEC, molten salt has relatively high efficiency and a high generation rate by chemical absorption and physical dissolution of carbonates, hydroxides or chlorine, CO₂ in such cells often exists as CO₃²⁻ which makes easy to remove CO, H₂ and other gaseous products from reactants¹⁶. Besides a wide electrochemical window, high electric conductivity, relatively low cost and their reactivity with CO₂, the possibility of carbon or CO hydrogenation after electrolysis in molten salts is much more significant. Molten salts, therefore, can be employed to convert CO₂ electrochemically to hydrocarbon gas to liquid fuels using renewable energy¹⁷. Moreover, Cherry and his research group¹⁷ reported different carbonates eutectics Li₂CO₃-K₂CO₃ (62–38%) and Li₂CO₃-Na₂CO₃ (52–48%) using a gold flag as the electrode at 575–650 °C to produce CO and H₂. Formation of 45.9% methane and 53.1% hydrogen has been shown by using molten carbonates Li_{0.43}Na_{0.26}K_{0.21}CO₃ (61:22:17) mixed with LiOH were used at 550°C using Ni wire as anode and iron wire as cathode using partitioned cell¹⁶. LiOH-LiCl at 380 °C reported as a promising technique for hydrogen supply, however, lack of efficient recycling of by-product has been a limitation to its use. A high yield 63.34% CH₄ and 35.81% H₂ formation have been reported using Fe cathode and Ni anode in Li_{0.85}Na_{0.61}K_{0.54}+0.15Ca(OH)₂ at 575°C and it is also found that replacing LiOH in place of calcium gives 24.36% CH₄¹⁸.

Despite molten salts types the electrolyser arrangement, electrodes, the variable conditions such as temperature, CO₂/H₂O ratio, effects significantly in the conversion of CO₂ to CO and hydrogen. Different electrolyser arrangements have been reported in the literature the electrolysis cell for CO₂ reduction to CO at 900° C using a partitioned compartment for each of the cathode and anode gas products has been reported¹⁹. Otake et al.,²⁰ demonstrated a direct reduction of carbon dioxide to CO using molten chloride with molten oxide in partitioned cell electrolyser. Many researchers

have also discussed the effect of different electrodes for hydrogen production as Hu et al.,²¹ discussed the electrode kinetics of nickel porous electrode for hydrogen production in molten carbonate electrolysis cell within the temperature range of 600–650°C.

However, the use of the same electrolyzer arrangement has not been reported for different molten salts. Herein, a new electrolytic cell using partitioned cell approach with ceramic tubes for collection of anodic and cathodic gases has been arranged to generate hydrocarbons using the eutectic mixtures including carbonates ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$; 43.5:31.5:25 mol%), chlorides (KCl and LiCl; 41-59 mol%) hydroxide (LiOH-NaOH; 27;73 and KOH-NaOH; 50:50 mol%). For the first time, the effect of feed gas ratio $\text{CO}_2/\text{H}_2\text{O}$ at different temperature (425 and 500°C) on electrolysis in molten salt has been taken into consideration. In this study different optimum conditions including the feed gas ratio $\text{CO}_2/\text{H}_2\text{O}$ (9.2 and 15.6), temperature (275–500°C) and applied voltage (1.5–3V) have been discussed based on the hydrocarbon product content and current efficiency. In addition, the effect of different cathode materials, titanium and mild steel in molten carbonates at 500°C with $\text{CO}_2/\text{H}_2\text{O}$ ratio of 15.6 in feed gas has also been discussed.

2 Material and methods

2.1 Chemicals

Lithium chloride (LiCl; 99%), potassium chloride (KCl; >99.9%), lithium hydroxide (LiOH; $\geq 98\%$ powder), sodium hydroxide (NaOH; $\geq 98\%$ pellets), potassium hydroxide (KOH; 90% flakes), sodium carbonate (Na_2CO_3 ; $\geq 99.5\%$), lithium carbonate (Li_2CO_3 ; $\geq 99.0\%$) and potassium carbonate (K_2CO_3 ; $\geq 99.0\%$) were procured from Sigma-Aldrich, USA. Carbon dioxide (CO_2 ; 99.99%) and argon (Ar; 99.99%) were supplied by Air products.

2.2 Reactor design

The Electrochemical measurements were carried out in house built cylindrical retort comprising of flange type cover using 316- grade stainless steel (17% Ni, 12% Cr, and 2% Mo) to shape the reactor. The dimensions of the retort were 130 mm internal diameter, 7.5 mm wall thickness and 800mm vertical length. A cooling water jacket (Height: 65 mm; Diameter: 200 mm; Thickness: 10 mm) was manually welded to the retort with the flange. On the flange cover, there were some holes drilled for the insertion of ceramics tube. Ceramics tubes are used to collect anode and cathode gases from electrode surface exposed to the molten salt and to guide the gas moving out of the reactor (**Fig. 1**). Two silicon rubber bungs served to hold electrodes inside the ceramic tubes. Another hole in the retort lid was used to insert a smaller ceramic tube for gas feed inlet, the tube was long enough to reach the surface of the molten salt contained in an alumina crucible.

The rotameters of flow range from 20 to 200 mL/min and 5 to 100mL/min at ambient temperature and pressure were connected with the cylinders of CO₂ (99.99%) and Ar (99.99%) that were set to 0.12 MPa. To obtain the desired content of steam (water vapour) in the gas inlet of the reactor, CO₂ and Ar were mixed together before introducing to a dreschel bottle containing 100 mL Millipore grade deionised water. The outlet gas tube was connected to another dreschel bottle having Laboc 10 mineral oil to prevent air entry. A stainless steel stand (Height; 380 mm) was placed and a refractory brick was mounted. In this setup, parts of the cathode and anode rods were deliberately brought out from the tube end inside the salt^{19, 20, 22}. In this study combination of four molten salts were used as electrolytes a mixture of molten carbonates (Li₂CO₃-Na₂CO₃-K₂CO₃), a mixture of molten chlorides (LiCl-KCl) and two mixtures of molten hydroxides (LiOH-NaOH and KOH-NaOH).

The selection of the molten salt was done based on low melting points and 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. The electrolyte salts were dried at 200 °C for 4h at atmospheric pressure before their mixing to remove any sort of water impurity and then poured into a corrosion-resistant electrolyser's retort²³. Different electrode materials have been used for different molten salts, a graphite rod of 5 mm in diameter was used in molten chlorides whereas, a mild steel rod (BDMS, 5 mm diameter) was used as the cathode in both carbonate and hydroxide molten salts. A titanium foil of (25×100×1 mm) dimension and nickel rod of 5 mm diameter were used also as cathode materials in molten carbonate for the selective production of hydrocarbon species. A 6 mm diameter stainless steel rod (304 grade) was used as the counter electrode or anode in the case of both molten carbonate and hydroxide.

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 the transition metals such as Fe, Ni, Co, etc. inside molten chloride^{21, 23, 24}. Whereas the comparison between two different cathode materials titanium foil 1×20×100 mm³ and mild steel rod of 5 mm in diameter based on hydrocarbon product content was carried out for electrolysis in the mixed Li₂CO₃-Na₂CO₃-K₂CO₃ with 43.5-30.5-25 mol% at 500 °C, 1.5 V and a CO₂/H₂O ratio of 15.6 in the feed gas.

2.3 Characterization

The PerkinElmer Clarus 580 type instrument was used for gas chromatographic analysis (GC) of general light hydrocarbons ($<C_6$). The Clarus GC has an FID channel to analyse the hydrocarbon gases and the non-hydrocarbon gases were analysed using TCD detector. In this instrument, the gas separation was performed using an RT® Alumina Bond/KCl capillary column (30 m \times 0.32 mm i.d., 5 μ m) with helium as the carrier gas for hydrocarbon analysis and a Haysep N6 packed column (60–80, 7' \times 1/8" 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^{25, 26}.

The gas samples were identified and quantified by comparing two different gas calibration standards first which have permanent gas standard with composition of H₂ 10%, CO₂ 10% and CO 40% for TCD detector and the second standard calibration gas for the FID detector contains ethane (C₂H₄) 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%. To analyze the feed gas compositions for CO₂ and H₂O contents gas detecting tubes from GASTEC (ai-cbss Ltd.) were used. With the change in colour from orange to yellow, GASTEC 2HH is characterized to detect the higher contents of CO₂ from 5 to 40% of the feed gas. The water content in the range of 0–18 mg/L can be analyzed by using GASTEC30 tube, and it contains Mg(ClO₄)₂²⁷.

3 Results and discussion

3.1 Analysis of electrolyte selection

The molten salt used for electrolysis should possess the ability to be used at low operating temperatures without solidification in order to perform the process in the liquid state. Moreover, salt should have high CO₂ capturing capacity and sufficiently negative cathodic limit in terms of the individual reduction of CO₂ and H₂O to CO and H₂ respectively²⁸.

3.1.1 Molten Carbonates

The ternary mixture of Li₂CO₃-Na₂CO₃-K₂CO₃ (43.5, 31.5, and 25.0) mol% has been chosen as it provides the lowest melting point of 397°C amongst all forms of inorganic molten carbonates. The most attractive characteristic of molten carbonate salts, their high capacity for capturing CO₂²⁹.

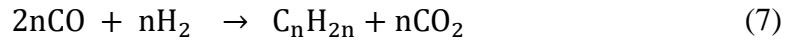
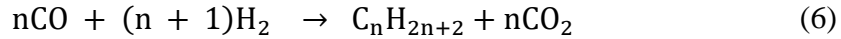
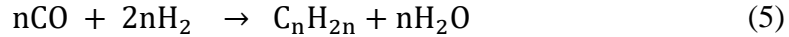
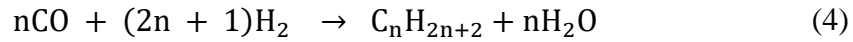
The production rates and selectivity for various hydrocarbon species and non-hydrocarbon species including (CH₄, C₂H₄, C₃H₆, C₄H₈, C₆H₁₄, C₇H₁₆, CO, H₂O, and H₂) were investigated in molten carbonates (Li₂CO₃-Na₂CO₃-K₂CO₃; 43.5:31.5:25 mol%) at 425 °C and 1.5 V by using the gas feed composition of 48.4% (CO₂) + 3.2% (H₂O) + 48.4% (Ar) at CO₂/H₂O=15.6 and titanium plate as a cathode with the surface area of 5.9 cm². The findings presented in **Fig. 2** and **Table 1** reported that the selectivity for different hydrocarbon species including CH₄, C₃H₆, and C₄H₈ was good at 425 °C due to the lower rates of H₂ and CO in the final products. The presence of CO as clearly noted from **Table 1** a relatively significant amount (in comparison to CH₄), can be imputed to the individual reduction of CO₂ to CO. On the other hand, some amount of CO₂ was detected in the product using a TCD detector for the non-hydrocarbon channel in the GC **Fig. 2**.

This is because some of the primarily absorbed CO₂ from the molten carbonates can be flushed from the molten salt surface inside the ceramic tube during electrolysis also, a ten-time higher calorific value as compared to H₂ and CO is offered by the formation of higher molecular weight products (such as C₆H₁₄ and C₇H₁₆) with small production rates (2.4 and 1.2 μmol/h cm² respectively). The formation of CH₄ can be justified by the reaction of carbon and carbon monoxide with hydrogen. The feasibility of the formation of methane gas from C, CO and hydrogen can be seen from **Eqs.(1) to (3)** as the change in Gibbs free energy at 425 °C is negative indicating the spontaneous reaction. Ji *et al.*,¹⁸ reported CO₂ reduction into CH₄ and H₂ at 575 °C using 20 cm² iron and Ni anode with a current efficiency of 92.97%. Wu *et al.*,³⁰ supported the conversion of CO₂ and H₂O to methane during molten carbonate electrolysis. Cherry *et al.*,¹⁷ claimed that the adsorption and formation of CO molecules can occur on the cathode by CO₂ reduction at low temperatures (≤650 °C), particularly with lower partial pressures of CO₂ less than 1 bar.



The formation of C₂H₆, C₃H₈ and C₄H₁₀ was relatively small compared with the corresponding alkenes (**Table 1**). This alkane formation can be confirmed in place of C₂-C₄ alkenes by mass spectrometric analysis (**Fig. 3**). Peaks 57, 43 and 29 stands for the mass of fragments lost .from C₄H₁₀ (CH₃CH₂CH₂CH₃), C₃H₈ (CH₃CH₂CH₃) and C₂H₆ (CH₃CH₃) respectively. The last peaks (43 and 29) are produced from the further fragmentation of C₄H₁₀ and C₃H₈.Peaks 55 and 41 stands

for the mass of fragments lost from 1-C₄H₈ (for instance) and C₃H₆ respectively. The higher intensity of 57 and 43 peaks in **Fig. 3** 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. The formation of alkene and alkane (C₂-C₄) can be seen from **Eqs. (4)-(5)**^{31, 32} and **Eqs.(6)-(7)**³³.



Due to the presence of CO in larger amounts as compared to hydrogen the formation alkene takes place. Generally, the alkenes and alkanes are formed from the CO₂ route because molten carbonates can absorb CO₂ produced during the reaction. The formation of alkenes as C₂H₄, C₃H₈, C₄H₁₀ at 425°C rather than alkanes occurs due to the partial oxidation of methane as can be seen from **Eqs. ((8)-(9))**.



The oxidation of methane can take place directly by the reaction with the oxygen produced from the anode or its oxygen absorbed inside the molten salt before passing through anode ceramic tube. On comparing the ΔG values of **Eqs.(1)to(3)** to that of **Eqs.(7) to (8)**, it can be concluded that the formation of higher hydrocarbon will be more feasible with alkenes being more favoured rather than alkanes.

3.1.2 Molten chlorides

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 production³⁴. The production rate of hydrocarbons was investigated in KCl-LiCl molten salt (41–59 mol %) which was continuously flowing through ceramic tubes at the conditions of atmospheric pressure, 2 V and 375°C using feed gas containing H_2O , CO_2 and Ar (97.9, 2.1 and 0%). The formation of CH_4 (0.05%) and H_2 (2.4–2.5%) gases were presented in **Fig. 4** The reaction of CO_2 with OH^- can be confirmed in the molten chloride for the as the concentration of CO_2 was only 4.8% and the faraday efficiency was found to be 59.3% as presented in **Table 2**.

Comparing the gas product results from the cathode in the molten carbonate with the molten chloride it can be seen that the molar ratio of H_2/CH_4 of product generated in the molten carbonates is about 24. This value is quite half of the ratio calculated for the molten chlorides. To increase productivity in case of molten chlorides high temperature and high voltages are required as reported by Ijjeet *al.*,³⁵ in case of carbon dioxide conversion using LiCl-KCl- $CaCl_2$ - $CaCO_3$ molten salt between the temperature range of 500 to 800 °C. Otake and his research group²⁰ also used LiCl

for the electrolysis of CO₂ at 650°C. This can be imputed to the higher formation of hydrocarbons in the molten carbonates rather than in the molten chlorides. 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%. Moreover, the energy consumption was found to be 311 J in case of chlorides which is greater than that of molten carbonates. This can be imputed to the formation of CO in the molten carbonate case, increasing the opportunity of hydrocarbon formation (**Table 2**).

3.1.3 Molten hydroxides

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 which results in the production of carbonate ions that are listed as non-electroactive ions in a molten hydroxide¹⁸. The electrolysis is performed with LiOH-NaOH (27–73 mol%) and KOH-NaOH (50:50 mol%) molten salt at 2 V applied voltage and at 275 °C with a gas feed (17% CO₂ + 3.1% H₂O by volume). **Table 3** shows a temperature effect on the production of methane, hydrogen and carbon monoxide during the electrolysis of LiOH-NaOH at 2.0 V cell voltage using the composition of CO₂, H₂O, and Ar in the feed. Due to the lower melting point (187 °C) KOH-NaOH salt was used at 220°C instead of 1LiOH-NaOH eutectic mixture.

Table 3 reported that at the constant voltage on increasing the temperature from 220 to 275 °C the H₂ production rate became slightly higher and there was a significant drop to 41.6 μmol/h.cm² at 335 °C. However, in molten KOH-NaOH (50:50 mol%) and LiOH-NaOH (27:73 mol%) salts the

production rates for CO and CH₄ were same as 0.00 and 6.12 μmol/hcm² when temperature increased from 220 to 275 °C and then inclined to 0.8 μmol/h cm² for both fuels at 335 °C in molten hydroxide. It has been suggested that hydrocarbon, H₂ and CO content does not improve by increasing the electrolytic temperature, in molten hydroxides (KOH-NaOH 50:50 mol%, and LiOH-NaOH 27:73 mol%). Liu *et al.*,²⁴ revealed that hydrogen formation increases slightly on increasing the temperature due to activity growth while CO decreases due to oxidation. **Fig. 5** confirms the formation of a gaseous product (CH₄, H₂, O₂, and CO₂) from the GC analysis by using FID and TCD detectors. Ji *et al.*,¹⁶ confirm that CH₄ and syngas are formed due to the co-electrolysis of C⁴⁺ and H⁺ in case of molten hydroxide, However, on comparing **Table 1** and **Table 3** it can be concluded that the current efficiencies and the gas product specification are better in molten carbonates than molten hydroxides at low temperature. CH₄ was the main products in case of molten hydroxide while other hydrocarbons such as propane, butane and hexane are not found due to lack of partial oxidation **Fig. 5**.

3.2 Optimization of electrodes

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 catalyzing 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 molten carbonate^{16-20, 22}.

A mild steel rod of 5 mm in diameter was used as a cheaper cathode material for electrolysis in the mixed $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ with 43.5-30.5-25 mol% 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 . Some other unidentified species over C5 (retention times over 23 min) were found also by 0.06% of the entire gas product.

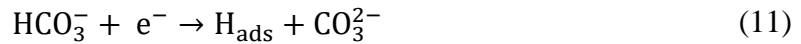
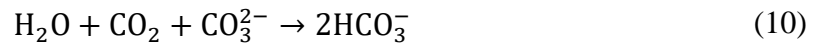
A titanium foil $1 \times 20 \times 100 \text{ mm}^3$ was used as an alternative cathode material for comparison. It was found that the content of C2-C5 species in the gas product in the titanium cathode material case was reduced by 50 to 0.015% while there was an increase in components over C5 by more than 65% over the previous value for mild steel to reach almost 0.1% of the whole gas product. Kalpan *et al.*,¹⁹ confirms that at higher temperatures titanium cathode is insoluble in carbonate molten salt and also does not form an alloy with the lithium, therefore can be used as a cathode for hydrocarbon fuel production using molten carbonate salt. Ossama *et al.*,³⁶ used Ti cathode for molten carbonates and confirmed the formation of higher hydrocarbons. Further, the GC analysis of both the cathode material **Fig. 6** revealed that the products in the case of titanium cathodic materials 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. These findings correlate with the literature⁹.

Siambun *et al.*³⁷ revealed that some amount of carbon formed during electrolysis penetrates in the steel cathode. In order to maintain carbon atom flux in mild steel, a pure carbon layer is important till the end of electrolysis. This thickness depends on two factors: carbon penetration rate and

carbon deposition rate. The penetration rate of carbon is controlled by diffusion and does not depend on applied voltage and temperature. While the carbon deposition rate is controlled by applied cell voltage. Due to the higher deposition rate, the penetration rate decreases as the deposit layer becomes thicker with time, therefore utilization of carbon is incomplete and hence, low amount of hydrocarbon products. Therefore, the titanium foil is found to be a better cathode material in case of molten carbonates rather than mild steel **Fig. 6**.

3.3 Effect of gas feed composition and temperature

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 molten carbonates, the mechanism of atomic (**Eq.(10)** and **Eq. (11)**) hydrogen formation can only be applicable if the concentration of CO₂ gas is less than 25% of the whole gas inlet.



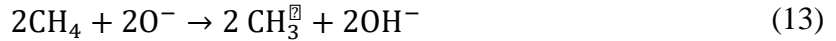
Regarding hydrocarbon formation, there are two possible mechanisms. The first mechanism is the combination of carbon deposited from CO₂ reduction with the above adsorbed hydrogen (**Eq.(12)**)



where C_xH_y represents the hydrocarbon formula and can be an alkane, alkene or any other type of hydrocarbon molecule. Such produced hydrocarbon fuels can be removed easily from the molten salt using a carrying gas such as argon, CO_2 or H_2O or flushed with the feed gas itself through the ceramic tube. The second possible mechanism is the partial oxidation of methane produced by **reaction with** C_2 -hydrocarbons as shown in **Eq. (13)**.



Therefore, in this case, the melt is a more basic and active form of oxide ions such as peroxide (O_2^{2-}) or superoxide (O^-) present in the basic melt and will play a significant role to perform C_2 gas formation according to **Eqs. (13) to (14)**.



It can be concluded that using a lower CO_2 content in the feed gas (10-25%) in molten carbonates will contribute to higher hydrocarbon formation in terms of higher oxobasicity (**Eq. (16)**) or from the feasibility of H_2 or H formation.



For the molten chloride case, as the minimum concentration of H_2O should be used, CO_2 gas can be introduced at higher concentrations (>90%) of inlet gas to ensure the high yield of CO or carbon in the product²⁰. For molten hydroxide though, CO_2 must be applied with lower concentrations (<10%) of inlet gas to reduce the carbonate ion formation²⁴. In this research, it was found (with regards to H_2O content) that using a CO_2/H_2O ratio between 10 and 15 in the feed gas would result

in higher current efficiencies. 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 synthesized under higher temperatures (>800 °C) ¹⁶.

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 **Fig. 7** 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. 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) (**Fig. 8**). 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, it was found that CH₄ amount produced at CO₂/H₂O=9.2 at 425 °C was quite high rather than other hydrocarbons due to high rate of H₂O reduction to hydrogen and lowering the feasibility of hydrocarbon formation.**

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 literature³⁰. The predominance of CH₄ production was very clear among other hydrocarbon species in this case (**Fig. 8**). 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 ($<500^{\circ}\text{C}$)¹⁷. Therefore, there is a clear relationship between the production rate of H_2 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 $\text{CO}_2/\text{H}_2\text{O}$ ratio of 15.6 at 500°C (**Fig. 7**).

On increasing the temperature to 500°C , an increase in H_2O in the gas feed does not lead to higher H_2 production rates like that in the case of 425°C possibly because H_2O solubility is lower, and HCO_3^- ions reduction that were formed from H_2O conversion to H_2 . It was recorded that CO_2 solubility increased in the molten carbonates by increasing the temperature whereas, the H_2O solubility was lower. Therefore, partial oxidation of CH_4 can occur even at $\text{CO}_2/\text{H}_2\text{O}$ ratio of 9.2. The higher hydrocarbon formation in the case of $\text{CO}_2/\text{H}_2\text{O}=15.6$ is because of the high partial pressure of carbon dioxide which leads to high deposition of CO_2 at the cathode as Ijije *et al.*,³⁵ confirmed it. Cherry and his research group¹⁷ showed with increase in CO_2 partial pressure both cathodic peaks and current densities increased, the partial pressure dependencies were also confirmed by Hu *et al.*,³⁸

3.3.1 Current efficiency

The optimization of each electrolyte can be done in the gas feed introduction method (GFOE and GFIE) for obtaining more fuel production. The formation of hydrocarbon species increases the combined current efficiency of cathodic products. It can be noticed from **Fig. 7** 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. Ijije *et al.*,³⁵ confirm that the current efficiencies were found to be 95% using molten carbonates at different temperature. 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 (**Fig. 9**). Therefore, the combined current efficiency of hydrocarbon products increased from 55 to 92% at this stage in contrast with the efficiencies of H₂ and CO which remained reduced. Ji *et al.*,¹⁸ confirmed the current efficiency was found to be 93% in the molten carbonates at 500°C and 1.8V.

However, the total current efficiency of the entire cathodic product reduced clearly from 95 to 79% by increasing the temperature under a CO₂/H₂O ratio of 9.2 due to the reduction of hydrocarbon generation in this case, despite the formation of C₇H₁₆ (**Fig. 7**). This is because increasing the temperature in case of CO₂/H₂O ratio of 15.6 there was a drastic increase in the formation of C₆H₁₄ and C₇H₁₆ while on increasing the temperature when CO₂/H₂O ratio is 9.2 CH₄ decreases and C₇H₁₆ was formed but not up to that extent. Alternately, the combined current efficiencies of the hydrocarbon species (due to C₇H₁₆ formation), increased from 12% at 425 °C to 24% at 500 °C (**Fig. 9**). Subsequently, the plot of current efficiencies with temperatures (**Fig. 9**), offers another proof for confirming the optimum conditions for hydrocarbon formation at 500°C under a molar ratio of CO₂/H₂O of 15.6.

4 Conclusions

In the present electrochemical system, molten salt electrolyser used included ceramic tubes for collecting the cathodic and anodic gases in molten carbonates (Li₂CO₃-Na₂CO₃-K₂CO₃; 43.5:31.5:25 mol %), hydroxide (LiOH-NaOH; 27; 73 and KOH-NaOH; 50:50 mol %) and chlorides (KCl-LiCl; 41-59 mol %) to investigate the formation of hydrocarbon fuel using different electrode material. Mass spectroscopy in the case of molten carbonate confirmed the formation of many hydrocarbon species (CH₄, C₂H₄, C₄H₈, C₇H₁₆) along with CO and H₂. The formation of

alkene was found in case of molten carbonates at 425°C and CO₂/H₂O ratio of 15.6. The production of CH₄ was found to be 0.67 μmol/h.cm² and H₂ 32 μmol/h.cm² using KCl-LiCl (41-59 mol%). Apart from hydrocarbon content, the current efficiency for molten carbonates was 99% while for molten hydroxide and molten chloride the value comes out to be 87.7% and 59.3% respectively. The GC results for CO₂/H₂O ratio of inlet gas reported that H₂ and CH₄ were the predominant product at lower CO₂/H₂O ratios (9.2) at 500°C in molten carbonates under 1.5V. However, the higher molecular hydrocarbon products (C₆H₁₄, and C₇H₁₆) were generated when electrolysis was carried out at higher ratios of CO₂/H₂O (15.6) in the feed gas at 500°C. The GC results for the effect of cathode material in molten carbonates showed 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. However, it is recommended to analyze the effect of anode material in the case of molten carbonates. While the study of the effect of electrode material, feed gas ratio can also be performed for hydroxides and chlorides for better results.

Acknowledgement

The authors are grateful for the financial supports from the EPSRC (EP/J000582/1 and EP/F026412/1), and Ningbo Municipal People's Governments (3315 Plan and 2014A35001-1).

References

1. Lei, L.; Liu, T.; Fang, S.; Lemmon, J. P.; Chen, F., The co-electrolysis of CO₂-H₂O to methane via a novel micro-tubular electrochemical reactor. *Journal of Materials Chemistry A* **2017**,5 (6), 2904-2910.
2. Lelieveld, J.; Klingmuller, K.; Pozzer, A.; Burnett, R. T.; Haines, A.; Ramanathan, V., Effects of fossil fuel and total anthropogenic emission removal on public health and climate. *Proceedings of the National Academy of Sciences of the United States of America* **2019**,116 (15), 7192-7197.
3. Abolfazl Irvani, M. h. A., Mahmood Zohri, Advantages and Disadvantages Of Green technology: Goals ,Challenges and Strengths. *International Journal of Science and Engineering Applications* 6 (09).
4. Gielen, D.; Boshell, F.; Saygin, D.; Bazilian, M. D.; Wagner, N.; Gorini, R., The role of renewable energy in the global energy transformation. *Energy Strategy Reviews* **2019**,24, 38-50.
5. Nanda, S.; Reddy, S. N.; Mitra, S. K.; Kozinski, J. A., The progressive routes for carbon capture and sequestration. *Energy Science & Engineering* **2016**,4 (2), 99-122.
6. Ahmed, R.; Liu, G.; Yousaf, B.; Abbas, Q.; Ullah, H.; Ali, M. U., Recent advances in carbon-based renewable adsorbent for selective carbon dioxide capture and separation-A review. *Journal of Cleaner Production* **2020**,242, 118409.
7. Christopher Graves , S. D. E., Mogens Mogensen, Co Electrolysis of CO₂ and H₂O in solid oxide cells : Performance and durability. *Solid State Ion* **2011**,192, 398-403.
8. Dincer, M. A. a. I., A review on photoelectrochemical hydrogen production systems : Challenges and future directions. *International journal of hydrogen energy* **2018**,44, 2474-2507.
9. Al-Juboori, O.; Sher, F.; KHALID, U.; Niazi, M. b.; Chen, G. Z., Electrochemical production of sustainable hydrocarbon fuels from CO₂ co-electrolysis in eutectic molten melts. *ACS Sustainable Chemistry & Engineering* **2020**.
10. Chen, Y.; Li, C. W.; Kanan, M. W., Aqueous CO₂ reduction at very low overpotential on oxide-derived Au nanoparticles. *Journal of the American Chemical Society* **2012**,134 (49), 19969-72.
11. Bevilacqua, M.; Filippi, J.; Miller, H. A.; Vizza, F., Recent Technological Progress in CO₂Electroreduction to Fuels and Energy Carriers in Aqueous Environments. *Energy Technology* **2015**,3 (3), 197-210.
12. Deka, D. J.; Gunduz, S.; Fitzgerald, T.; Miller, J. T.; Co, A. C.; Ozkan, U. S., Production of syngas with controllable H₂/CO ratio by high temperature co-electrolysis of CO₂ and H₂O over Ni and Co- doped lanthanum strontium ferrite perovskite cathodes. *Applied Catalysis B: Environmental* **2019**,248, 487-503.
13. Wang, Y.; Liu, T.; Lei, L.; Chen, F., High temperature solid oxide H₂O/CO₂ co-electrolysis for syngas production. *Fuel Processing Technology* **2017**,161, 248-258.
14. Zhang, X.; Song, Y.; Wang, G.; Bao, X., Co-electrolysis of CO₂ and H₂O in high-temperature solid oxide electrolysis cells: Recent advance in cathodes. *Journal of Energy Chemistry* **2017**,26 (5), 839-853.
15. Mehrshad Kamali Khameneh , A. B., Co-electrolysis of CO₂ , H₂O on LaFe_{0.6}Co_{0.4}O₃ promoted La_{0.75}Sr_{0.25}Cr_{0.25}Mn_{0.5}O₃/YSZ electrode in solid oxide electrolysis cell. *Electrochimica Acta* **2019**.

16. Ji, D.; Liu, Y.; Li, Z.; Yuan, D.; Yang, G.; Jiang, M.; Wang, Y.; Yu, Y.; Wu, H., A comparative study of electrodes in the direct synthesis of CH₄ from CO₂ and H₂O in molten salts. *International Journal of Hydrogen Energy* **2017**,*42* (29), 18156-18164.
17. Chery, D.; Albin, V.; Lair, V.; Cassir, M., Thermodynamic and experimental approach of electrochemical reduction of CO₂ in molten carbonates. *International Journal of Hydrogen Energy* **2014**,*39* (23), 12330-12339.
18. Ji, D.; Li, Z.; Li, W.; Yuan, D.; Wang, Y.; Yu, Y.; Wu, H., The optimization of electrolyte composition for CH₄ and H₂ generation via CO₂/H₂O co-electrolysis in eutectic molten salts. *International Journal of Hydrogen Energy* **2019**,*44* (11), 5082-5089.
19. Kaplan, V.; Wachtel, E.; Gartsman, K.; Feldman, Y.; Lubomirsky, I., Conversion of CO₂ to CO by Electrolysis of Molten Lithium Carbonate. *Journal of The Electrochemical Society* **2010**,*157* (4), B552.
20. Otake, K.; Kinoshita, H.; Kikuchi, T.; Suzuki, R. O., CO₂ gas decomposition to carbon by electro-reduction in molten salts. *Electrochimica Acta* **2013**,*100*, 293-299.
21. Hu, L.; Lindbergh, G.; Lagergren, C., Electrode Kinetics of the Ni Porous Electrode for Hydrogen Production in a Molten Carbonate Electrolysis Cell (MCEC). *Journal of The Electrochemical Society* **2015**,*162* (9), F1020-F1028.
22. Laude, T.; Kobayashi, T.; Sato, Y., Electrolysis of LiOH for hydrogen supply. *International Journal of Hydrogen Energy* **2010**,*35* (2), 585-588.
23. Chen, X.; Zhao, H.; Xie, H.; Qu, J.; Ding, X.; Geng, Y.; Wang, D.; Yin, H., Tuning the preferentially electrochemical growth of carbon at the “gaseous CO₂-liquid molten salt-solid electrode” three-phase interline. *Electrochimica Acta* **2019**,*324*, 134852.
24. Liu, Y.; Yuan, D.; Ji, D.; Li, Z.; Zhang, Z.; Wang, B.; Wu, H., Syngas production: diverse H₂/CO range by regulating carbonates electrolyte composition from CO₂/H₂O via co-electrolysis in eutectic molten salts. *RSC Advances* **2017**,*7* (83), 52414-52422.
25. Moretti, P.; Germinario, G.; Doherty, B.; van der Werf, I. D.; Sabbatini, L.; Mirabile, A.; Sgamellotti, A.; Miliani, C., Disclosing the composition of historical commercial felt-tip pens used in art by integrated vibrational spectroscopy and pyrolysis-gas chromatography/mass spectrometry. *Journal of Cultural Heritage* **2019**,*35*, 242-253.
26. Buchalter, S.; Marginean, I.; Yohannan, J.; Lurie, I. S., Gas chromatography with tandem cold electron ionization mass spectrometric detection and vacuum ultraviolet detection for the comprehensive analysis of fentanyl analogues. *Journal of chromatography. A* **2019**,*1596*, 183-193.
27. Aizawa, H.; Kusakari, S.-i.; Yamada, K.; Noda, K.; Habe, H., Development of Organic Gas Sensor Using Quartz Crystal Microbalance Coated with Plasma-polymerized Films. *Sensors and Materials* **2020**,*32* (3), 1123.
28. Zhang, P.; Xiao, X.; Meng, Z. N.; Li, M., Heat transfer characteristics of a molten-salt thermal energy storage unit with and without heat transfer enhancement. *Applied Energy* **2015**,*137*, 758-772.
29. Campanari, S.; Chiesa, P.; Manzolini, G., CO₂ capture from combined cycles integrated with Molten Carbonate Fuel Cells. *International Journal of Greenhouse Gas Control* **2010**,*4* (3), 441-451.
30. Hongjun Wu, D. j., Lili Li, Dandan yuan, A New Technology for efficient, high yield CO₂ and H₂O transformation to CH₄ by Electrolysis in Molten Salt. *Advanced Material technology* **2016**.

31. Akhmedov, V. I. A., The role of CO₂ and H₂O in the formation of gas- oil hydrocarons: current performance and outlook. *J.Math* **2019**,*10* (6).
32. Torrente-Murciano, L.; Mattia, D.; Jones, M. D.; Plucinski, P. K., Formation of hydrocarbons via CO₂ hydrogenation – A thermodynamic study. *Journal of CO₂ Utilization* **2014**,*6*, 34-39.
33. Jafarbegloo, M.; Tarlani, A.; Mesbah, A. W.; Sahebdehfar, S., Thermodynamic analysis of carbon dioxide reforming of methane and its practical relevance. *International Journal of Hydrogen Energy* **2015**,*40* (6), 2445-2451.
34. Jiang, R.; Gao, M.; Mao, X.; Wang, D., Advancements and potentials of molten salt CO₂ capture and electrochemical transformation (MSCC-ET) process. *Current Opinion in Electrochemistry* **2019**,*17*, 38-46.
35. Ijije, H. V.; Lawrence, R. C.; Siambun, N. J.; Jeong, S. M.; Jewell, D. A.; Hu, D.; Chen, G. Z., Electro-deposition and re-oxidation of carbon in carbonate-containing molten salts. *Faraday discussions* **2014**,*172*, 105-16.
36. Al-Juboori, O.; Sher, F.; Hazafa, A.; Khan, M. K.; Chen, G. Z., The effect of variable operating parameters for hydrocarbon fuel formation from CO₂ by molten salts electrolysis. *Journal of CO₂ Utilization* **2020**,*40*, 101193.
37. Nancy J. Siambun, H. M., Di Hu, Daniel Jewell, Yeo K. Beng, and George Z. Chena,, Utilisation of Carbon Dioxide for Electro-Carburisation of Mild Steel in Molten Carbonate Salts *Journal of The Electrochemical Society* **2011**,*158*.
38. Lan Hu, z. G. o. L., and Carina Lagergren, Electrode Kinetics of the Ni Porous Electrode for Hydrogen Production in a Molten Carbonate Electrolysis Cell (MCEC) *Journal of The Electrochemical Society* **2015**,*169*.

List of Tables

Table 1. Specifications of the cathodic gas product during electrolysis using molten carbonates at 1.5 V and different temperature obtained from GC analysis.

Product	Gas Product Composition (vol %)		Product rate ($\mu\text{mol/h cm}^2$)		Selectivity (%)		Current efficiency (%)		Heating value (J)		Total energy Consumption (J)	
	425°C	500°C	425°C	500°C	425°C	500°C	425°C	500°C	425°C	500°C	425°C	500°C
5												
H ₂	0.22	0.210	4.40	4.00	-	-	11.90	5.10	11.40	7.30		
CH ₄	0.06	0.02	1.10	0.40	6.80	7.00	12.50	2.00	10.40	2.60	6	15
C ₂ H ₄	0.04	0.00	0.80	-	5.00	-	13.20	-	12.00	-	7	16
C ₃ H ₆	0.03	0.00	0.50	-	3.10	-	12.70	-	11.00	-	8	17
C ₄ H ₈	0.03	0.00	0.50	-	3.10	-	17.00	-	14.50	-		
C ₆ H ₁₄	0.00	0.12	-	2.40	-	42.10	31.80	58.00	35.30	75.00	9	18
C ₇ H ₁₆	0.00	0.06	-	1.20	-	21.00	-	32.40	-	43.30	114.20	171.00
CO	0.58	0.100	11.70	1.70	-	-	-	2.20	-	3.70	10	
CO ₂	52.70	40.30	-	-	-	-	-	-	-	-	11	
H ₂ O	2.40	3.10	-	-	-	-	-	-	-	-	12	
Ar	44.00	56.10	-	-	-	-	-	-	-	-	13	
											14	

Table 2. Cathodic product gas compositions and the current efficiency of the individual components after electrolysis in molten chlorides at different voltage and 375 °C.

Product	Gas Product Composition (vol %)		Product rate ($\mu\text{mol/h cm}^2$)		Current efficiency (%)		Total energy Consumption (J)	
	1.5V	2 V	1.5 V	2 V	1.5 V	2 V	1.5 V	2 V
H ₂	2.40	2.48	32.00	19.10	54.80	28.20		
CH ₄	0.05	0.05	0.67	0.38	4.50	2.30		
CO	0.00	0.00	0.00	0.00	0.00	0.00		
CO ₂	34.80	4.84	-	-	-	-		
H ₂ O	2.00	2.00	-	-	-	-	278.00	311.00
Ar	60.80	90.63	-	-	-	-		

Table 3. The cathodic gas product during electrolysis in the molten hydroxides at 2 V and different temperatures obtained from GC analysis.

Molten salt	Temperature (°C)	Product gas	Gas composition (Vol %)	Production rate (μmol/h cm²)	Current efficiency (%)	Total energy Consumption (J)
KOH-NaOH (50-50 mol%)	220	H ₂	3.94	164.70	15.60	1000.00
		CH ₄	0.15	6.12	2.30	
		CO	0.00	0.00	0.00	
		CO ₂	0.58	-	-	
		H ₂ O	0.00	-	-	
		Ar	95.30	-	-	
LiOH-NaOH (27-73 mol%)	275	H ₂	4.44	185.70	13.00	1200.00
		CH ₄	0.15	6.12	2.00	
		CO	0.00	0.00	0.00	
		CO ₂	0.75	-	-	
		Ar	94.70	-	-	

List of Figures

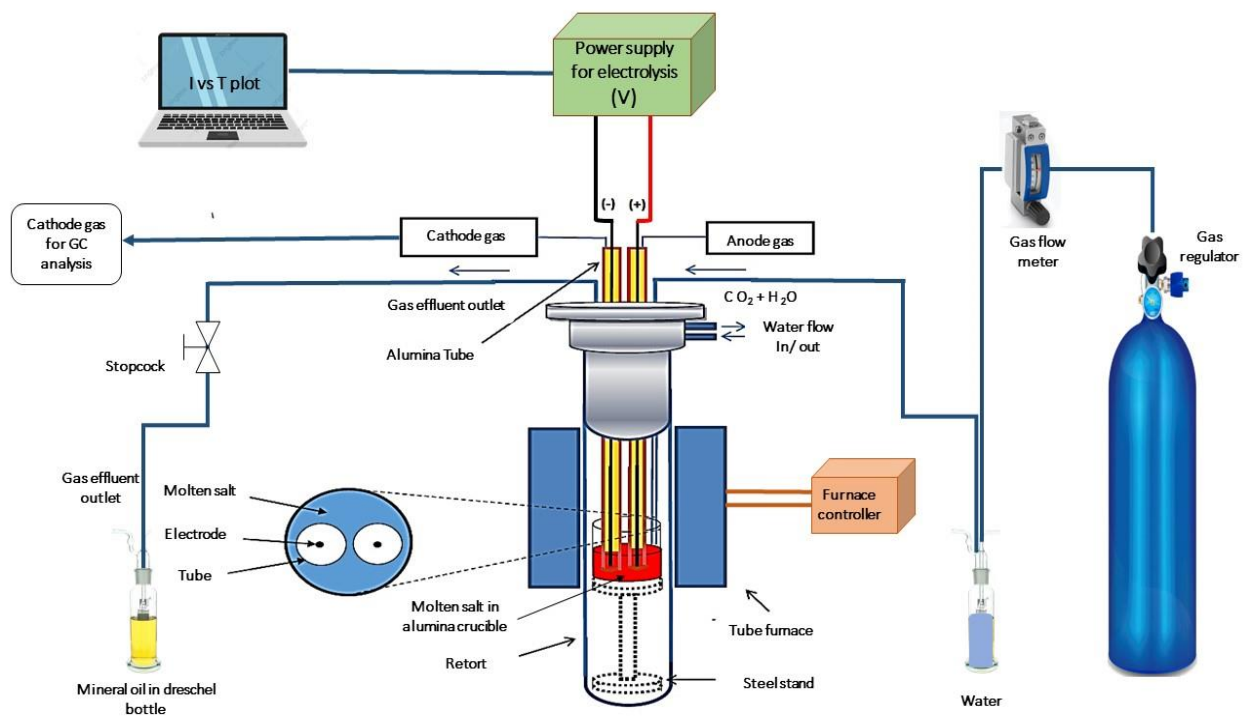


Fig. 1. The schematic representation of the electrolytic cell experimental setup.

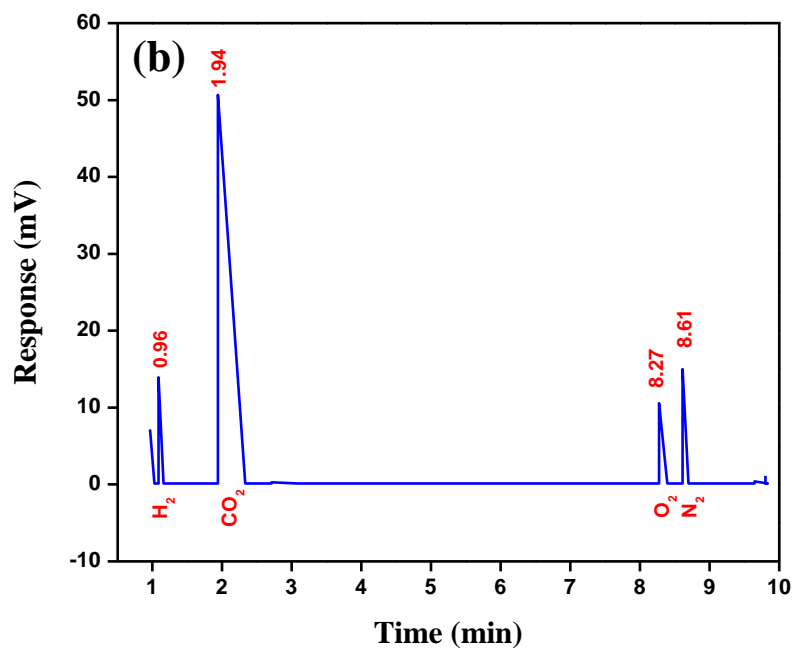
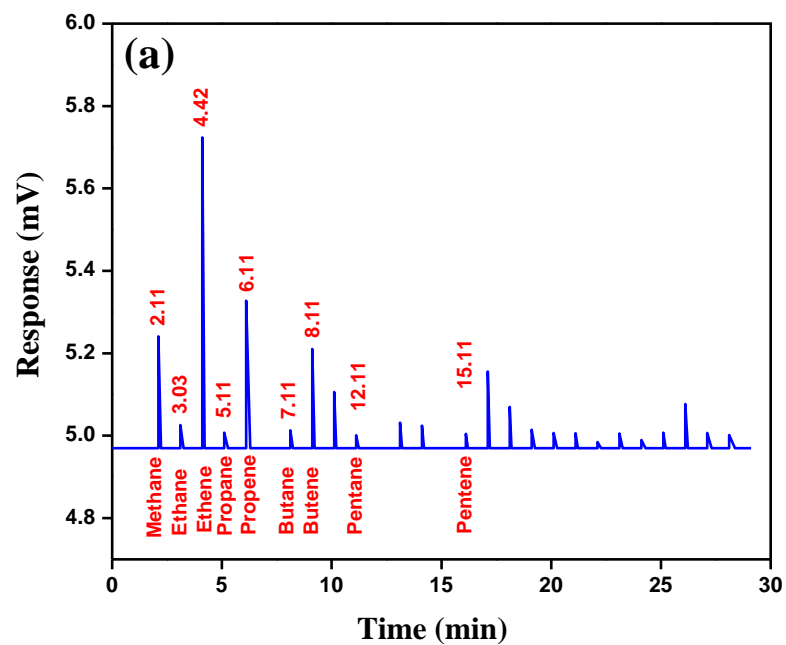


Fig. 2. The gas chromatography analysis of cathodic gas using molten carbonates at 1.5 V and 425 °C; (a) FID detector and (b) TCD.

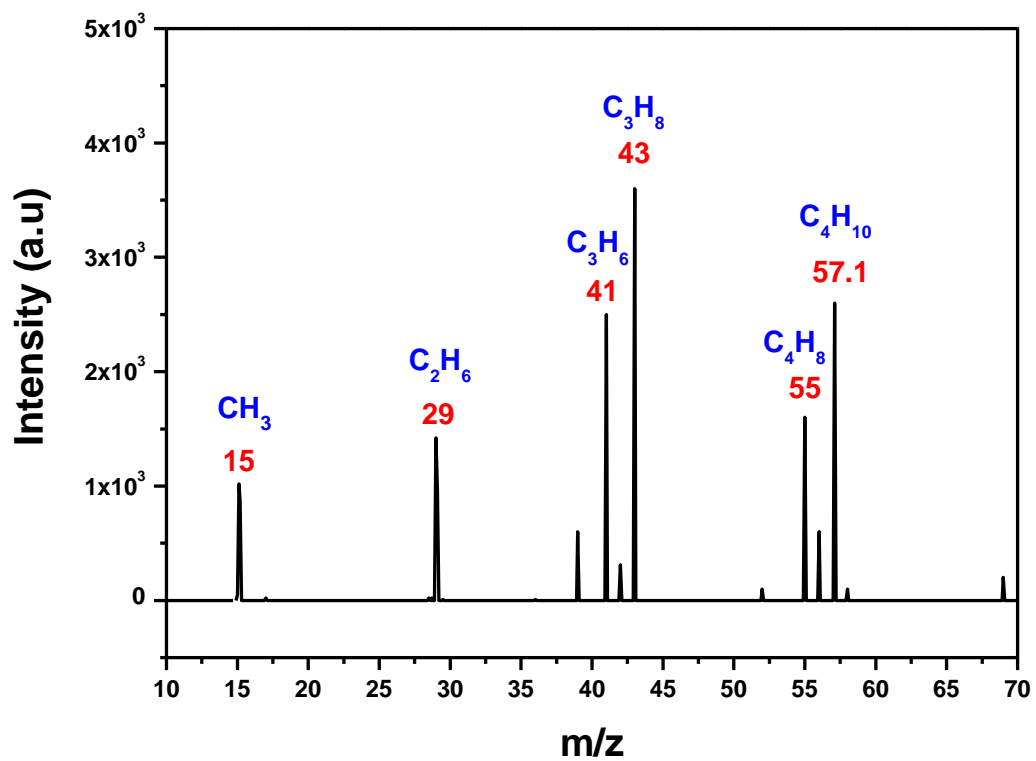


Fig. 3. Mass spectrum of compounds showing hydrocarbons after electrolysis in the molten carbonate electrolyte at 1.5 V at 425 °C.

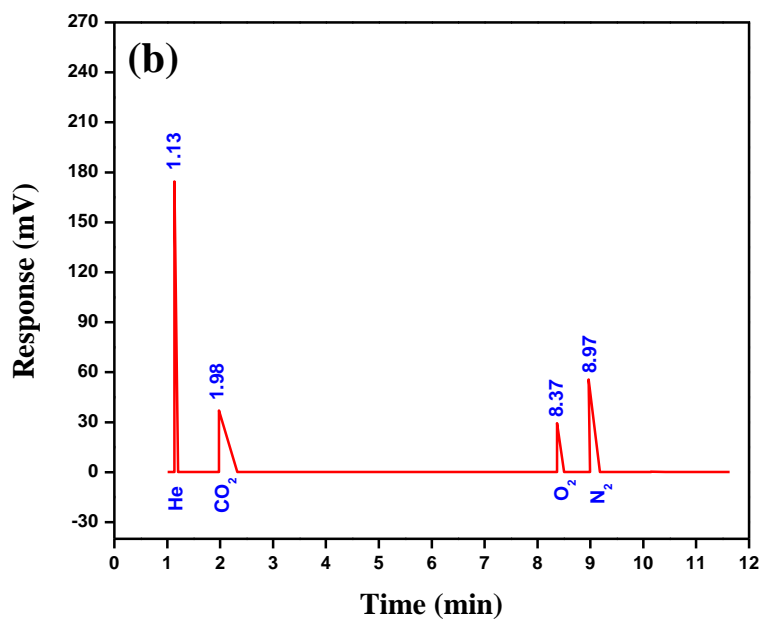
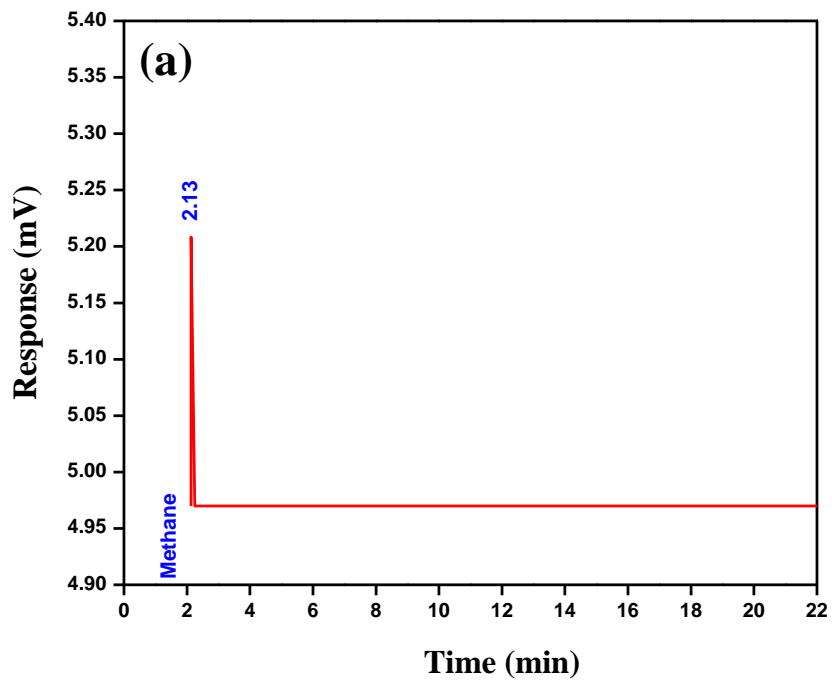


Fig. 4. The gas chromatography analysis of gaseous products in molten chlorides at 375 °C and 2 V; (a) FID detector and (b) TCD detector.

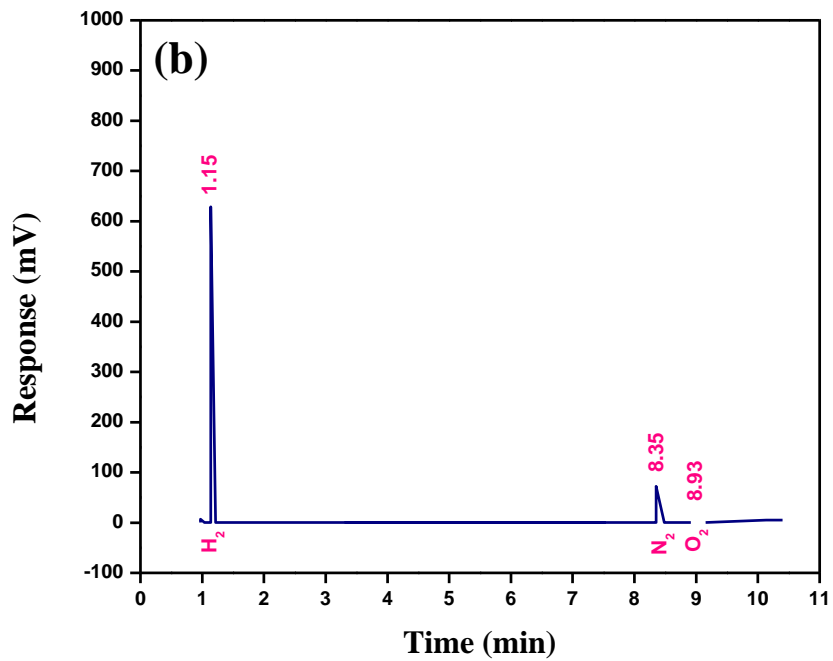
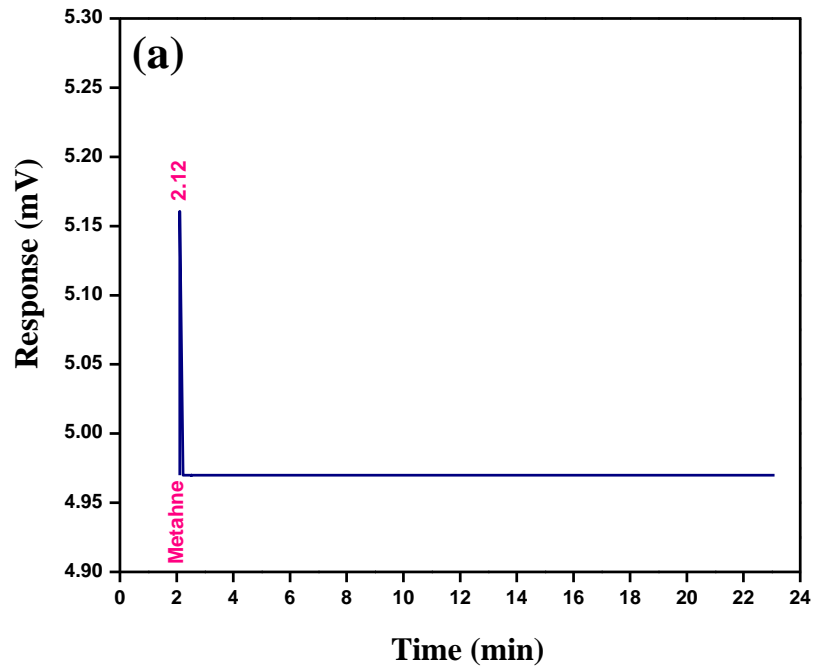


Fig. 5. Gas chromatography analysis of gaseous product in molten hydroxide at 2 V and 275 °C; (a) FID detector and (b) TCD detector.

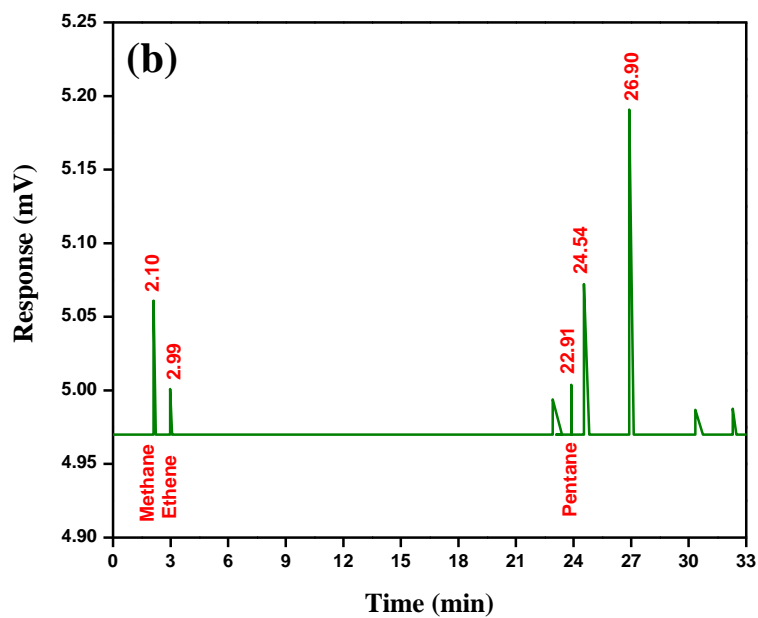
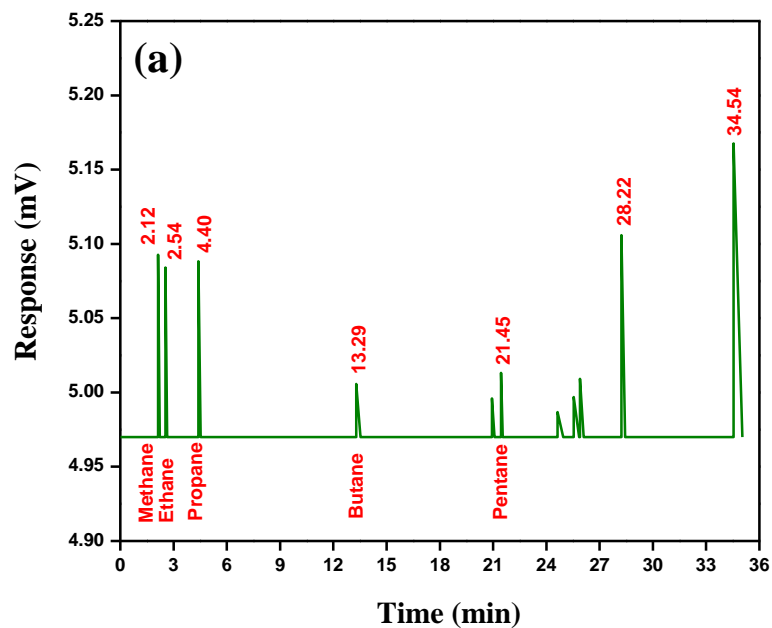


Fig. 6. FID detector analysis of gas sample during the electrolysis of molten carbonate using different cathode materials; (a) Mild steel and (b) Titanium foil.

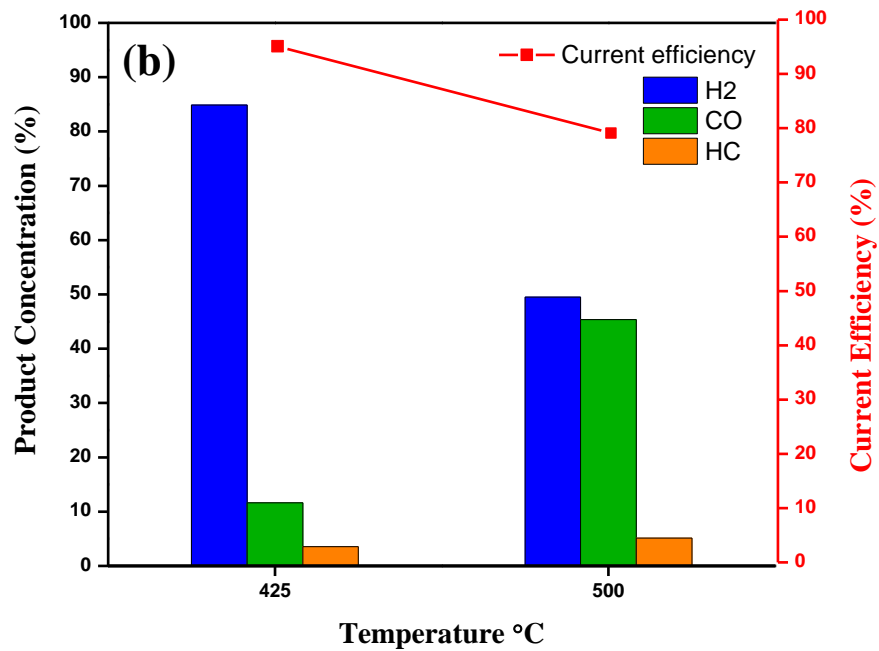
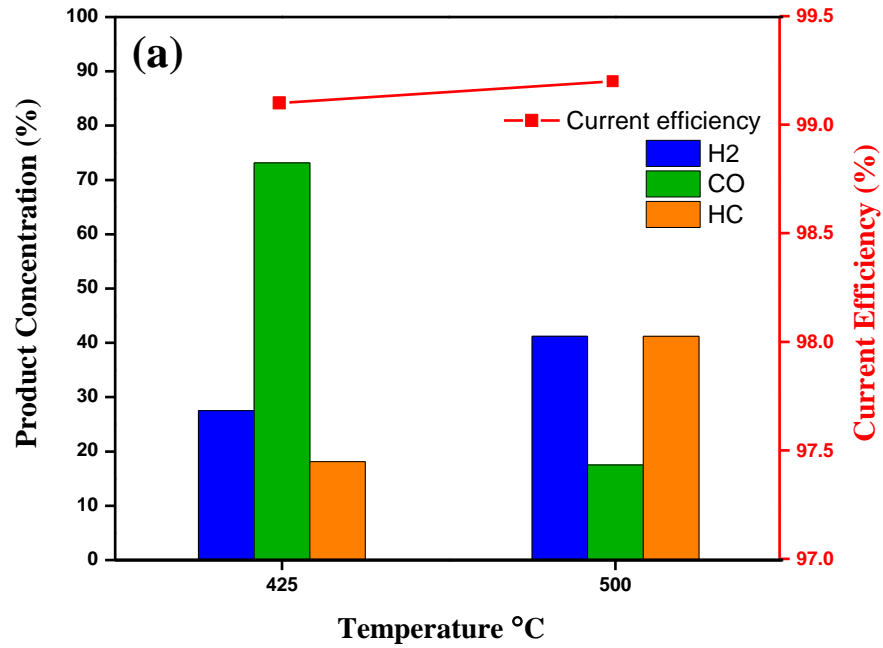


Fig. 7. Production rates and current efficiencies of CO, H₂ and hydrocarbons at two different temperatures obtained by electrolysis in ternary molten carbonates at 1.5 V and different CO₂/H₂O feed gas ratio; (a) 15.6 and (b) 9.2.

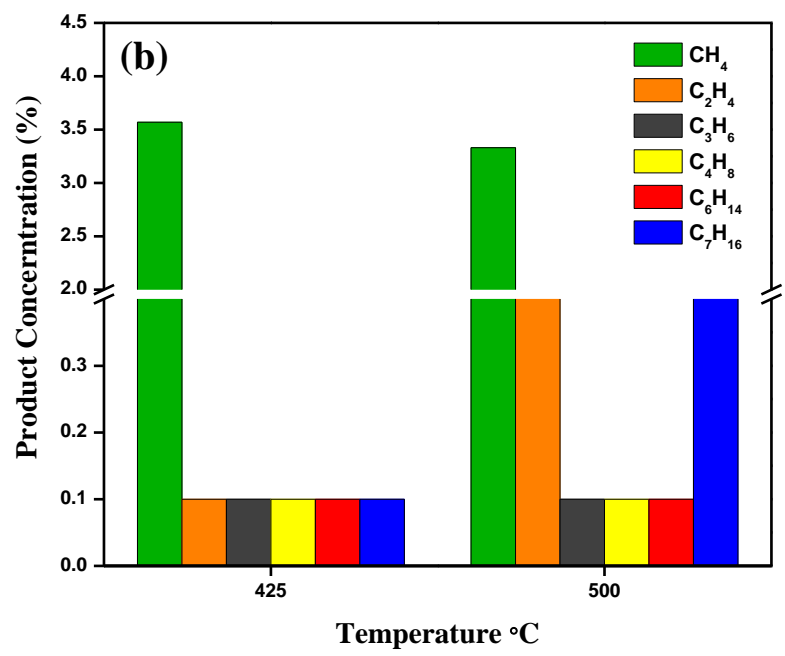
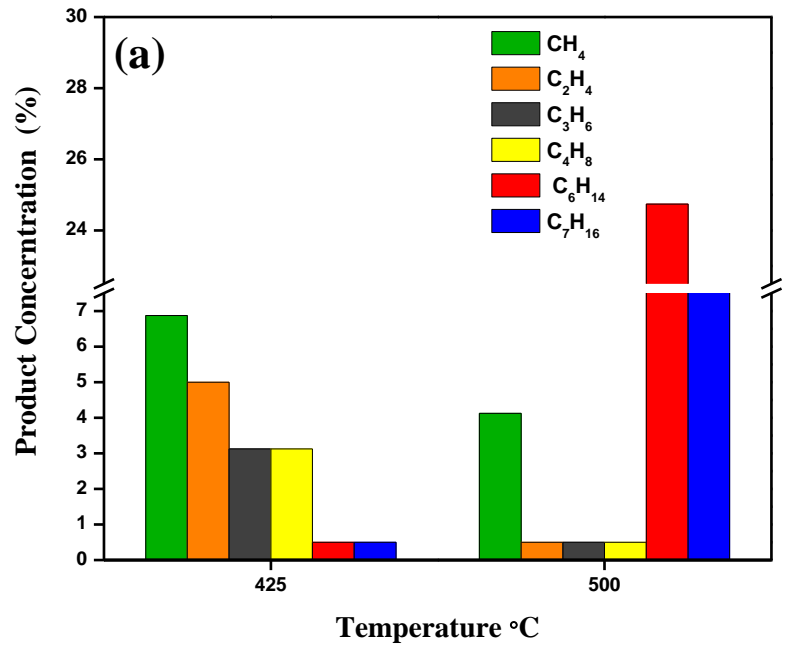


Fig. 8. Different hydrocarbon products obtained by electrolysis in ternary molten carbonates at 425 and 500 °C with different CO₂/H₂O feed gas ratio; (a) 15.6 and (b) 9.2.

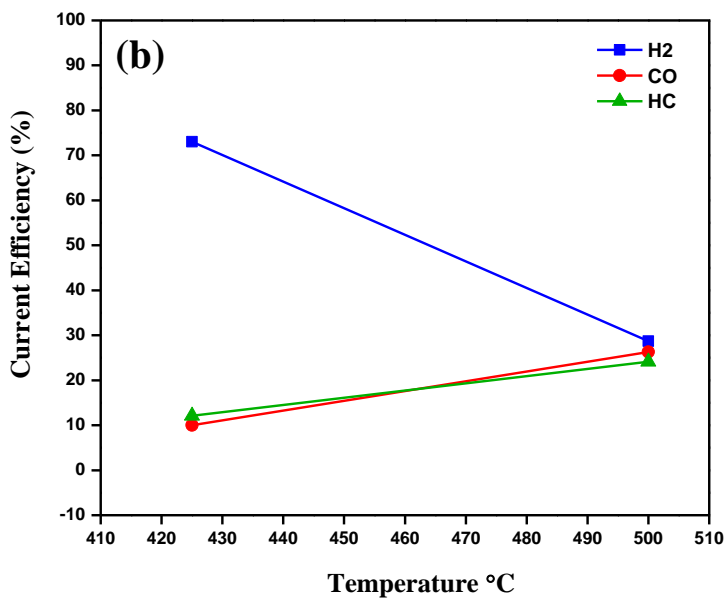
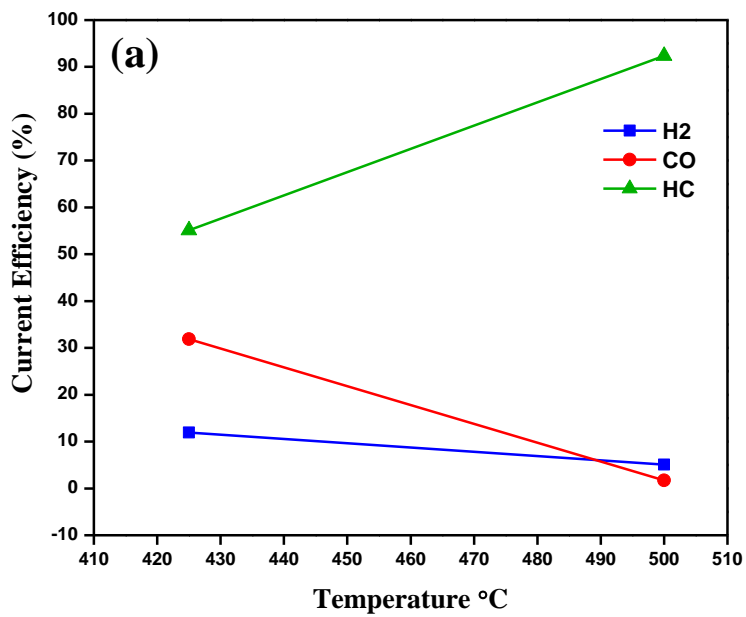


Fig. 9. Current efficiencies of CO, H₂ and hydrocarbon species at different temperature and constant applied voltage of 1.5V with different CO₂/H₂O feed gas ratio for molten ternary carbonates; (a) 15.6 and (b) 9.2.

For Table of Contents Use Only

Graphical Abstract

The electrochemical reduction of carbon dioxide and water was performed to generate hydrocarbon fuels using three types of molten eutectic-salt electrolytes.

