Investigation of pulsed electrolysis for choline-based deep eutectic solvents coupled with amines for integrated carbon dioxide capture and electrochemical conversion

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Abstract

Traditional carbon capture processes require large amounts of energy to regenerate the solvents used. Recent research has proposed to decrease the energy requirements of this process by integrating the system of carbon capture and electrochemical conversion, removing the need for the traditional regeneration step. The integration of these two steps involves the use of the same medium for both the carbon capture solvent and for the electrolyte for electrochemical conversion of the captured CO_2. The proposed methodology takes advantage of the inherent elevated temperatures resulting from ohmic losses in the electrochemical system, especially at an industrial scale and helps optimize the efficiency of the conversion process. This study investigates the use of non-aqueous solutions of 1:4 choline chloride to ethylene glycol coupled with monoethanolamine as the medium for this process, particularly focussing on its use as the catholyte in this system. Specifically, this project targets the production of carbon monoxide using silver cathodes in small laboratory scale compact H-cells, with an anolyte of 0.5 M sulphuric acid and a Nafion-117 cation exchange membrane separating the compartments. Different operating conditions, including pulsed electrolysis, are utilised to attempt to modify the levels of carbon monoxide production and stabilise the system for long term operation.

Initial investigations into this system found that carbon monoxide could successfully be produced at constant reduction potentials vs. Ag/AgCl of -1.5 V and -1.7 V for approximately 10 minutes of operation when operating at 65 °C. Pulsed electrolysis has been proven to be able to increase the stability of carbon monoxide production for up to an hour of operation. The study found that the most promising conditions for the pulsed electrolysis are using positive anodic potentials vs. Ag/AgCl of either + 0.1 V or + 1.5 V for between 5 and 40 seconds in combination with cathodic potentials vs. Ag/AgCl of - 1.5 V. The faradaic efficiency of carbon monoxide production was able reach up to 24 % for one hour of operation with relatively stable production profiles when using pulsed electrolysis.

The results of this project show that this system can produce the desired carbon dioxide reduction reaction and with the use of pulsed electrolysis this can be achieved for at least one hour with faradaic efficiencies of carbon monoxide production greater than 20%. These findings showed a better overview for the next stage of this research. In particular, further work involving longer term operation of the cells is of interest after this research.

Glossary

Abbreviation	**Definition**
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilisation
DEA	Diethanolamine
DES	Deep Eutectic Solvents
FE	Faradaic Efficiency
GC	Gas Chromatography
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
HER	Hydrogen Evolution Reaction
HPLC	High Performance Liquid Chromatography
ICP	Inductively Coupled Plasma
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
MEA	Monoethanolamine
OER	Oxygen Evolution Reaction

RWGS	Reverse Water Gas Shift
TEA	Triethanolamine

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1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) unequivocally states human activities are the leading drivers of global warming [7]. This change in the Earth's climate is primarily being driven by the emission of large volumes of greenhouse gases including Carbon Dioxide (CO_2) and methane [8]. These emissions are largely associated with the industrial processes that keep modern society functioning, including electricity generation, transport, and chemicals manufacturing [7]. Climate change is already having a widespread impact globally, with a recorded increase in average surface temperature of 1.09 °C since 1900 [7]. According to the IPCC, climate change has led to 'irreversible losses' in a wide variety of ecosystems and has contributed to a decline in global food security [7]. There is a consensus in the scientific community that action must be taken to limit human caused emissions and avoid additional irreversible damage to the environment and the climate [9].

The emissions of one of the most important greenhouse gas, CO2, reached a record amount of 36.8 Gt in 2022 from energy related processes alone [10]. As the world shifts to a more sustainable future, the challenges associated with the decarbonisation of the world's energy systems and industries are immense. In this regard, renewable energy such as wind and solar will undoubtedly play a major role in decarbonising both of these sectors. However, there are still certain industries that are very technically challenging to decarbonise [11]. One strategy to reduce the emissions of CO_2 from these industries involves implementing technologies to capture the CO_2 emitted by these processes. Captured CO_2 can then either be put into long term storage, utilised to form energy carriers, such as methanol or liquid hydrocarbons, or serve as feedstock for other industrial processes [11]. One particularly promising method of converting CO_2 into higher value chemicals is through electrochemical reduction, which has gained greater interest recently as a means to integrate renewable electricity into this system [12], [13].

The aim of this project is to investigate the use of new solvents in an integrated system of carbon capture and electrochemical reduction, using the same medium for both the capture process and the electrolyte in the electrochemical reduction. In recent years, this integrated approach has been proposed as a way to reduce the overall energy demand and costs of the system [14]. Traditional solvents for carbon capture, mainly aqueous amines, have long been industry standards due to their high loading capacity of CO_2 and ability to be regenerated for further use [15]. However, they come with inherent drawbacks, including corrosion of process equipment and high energy requirements for regeneration [16]. To address the limitations associated with aqueous amines, ongoing research is exploring new classes of solvents. One promising class of solvents are Deep Eutectic Solvents (DES), a mixture of chemicals which has a markedly reduced freezing point compared to its constituent parts [17]. Notably, there is significant interest in coupling these solvents with the standard aqueous amine solutions, giving the combined advantages of both the amine and DES . This project will investigate the viability of coupled amines and DES within this integrated system, with a particular focus on evaluating their performance in the electrochemical reduction process.

The main motivation for this project is to further develop specific areas of the key technology of Carbon Capture and Utilisation (CCU). The use of DES coupled with amines for this system is relatively unstudied. Filling in this gap in the literature is a key motivation for this project, as understanding how these new classes of solvents behave, and their stability is an important step towards rolling this technology out at an industrial scale. This is particularly interesting for the low carbon future as it is easier to integrate this system into renewable electricity production than traditional carbon capture and conversion technologies. This means that carbon producing industries could be integrated with renewable energy production, such as solar or wind, to produce sustainable fuel or chemicals.

The research questions for this project are outlined in Chapter 2. The background information for this project, including explaining what carbon capture is and the various routes that it can be achieved, is given in Chapter 3. In Chapter 4 a detailed literature review is carried out with the objective of determining a viable solvent for investigation in the subsequent experimental stages of this project, as well as identifying issues likely to occur with the system and strategies to combat them. Chapter 5 outlines the methodology employed for conducting the experiments in this project. The results are then presented in Chapter 6, with a discussion of these presented in Chapter 7. Lastly, the conclusions that can be drawn from this project and recommendations for further work are covered in Chapters 8 and 9 respectively.

2. Research Questions

The overall focus of this thesis is to investigate potentially promising solvents for use in the integrated system of carbon dioxide capture and electrochemical conversion processes. DES coupled with amines are particularly attractive for this system as they incorporate both chemical and physical absorption, and the DES helps to increase the electrical conductivity of the amine. This overall project is separated into several research questions.

1. Which DES and amine mixtures are likely to be suitable for use in electrochemical CO_2 reduction?
2. What process conditions are suitable for using this DES and amine mixture for CO_2 reduction in a H-cell?
3. What process conditions and electrochemical techniques can be used to ensure the system can operate long term?
4. How does the electrolyte used in this project compare to other electrolytes?

The first research question is designed to determine from literature several pieces of key information for the project. Firstly, the most suitable amine DES mixture needs to be found, with a focus on the electrical conductivity and the CO_2 loading capacity of the mixtures. Additionally, it needs to be determined from the literature at what conditions that this mixture may be able to produce the desired CO_2 reduction reaction. The second and third research questions are designed to first prove that the system is viable and then to find the optimal conditions for its use. These will be answered in the laboratory section of this project by running the system at various different operating conditions and analysing the products and the current response of the system. Particular focus will be placed on the stability of the different parameters analysed to see how well the system can maintain constant operation. Finally, all the results from this project will be compared to literature to determine if this system and the chosen solvents are indeed viable compared to industrial standard. It will also examine what further work needs to be done to allow for the scale up of this technology and what the main issues holding the system back from widespread use are.

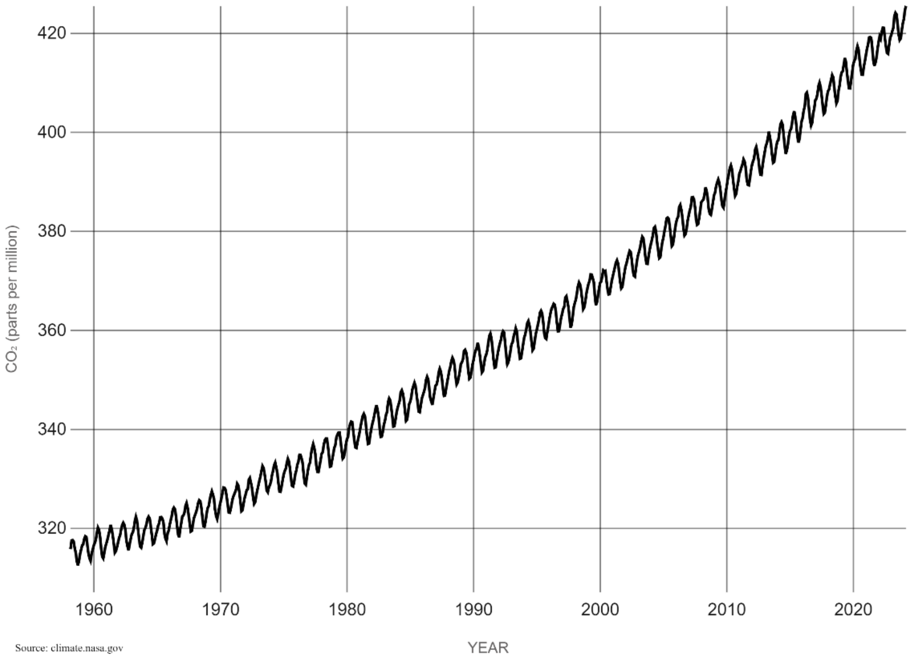
3. Background Information

The global economy is currently powered primarily by fossil fuels such as coal, oil, and natural gas, which has led to a rapid rise in the release of greenhouse gases, including CO_2 and methane [7], [18]. The increase in greenhouse gas concentrations in the atmosphere has directly contributed to climate change [7]. To mitigate environmental damage and address global climate concerns, the world is actively transitioning towards low or zero carbon power through renewable energy sources, such as solar and wind. However, other possible technologies to limit the CO_2 emissions have been put forward to work in conjunction with this transition to clean energy. One of the most interesting of these is CO_2 capture, also often called carbon capture. This chapter aims to provide an introduction to the key concepts associated with this research area and report. This includes an introduction to climate change and what is driving it, carbon capture technologies, and an introduction to Deep Eutectic Solvents (DES) and their application in this context.

3.1 Climate Change

Climate change is the global long-term shift in average temperatures and broader weather patterns [19]. These changes can be driven by natural cycles of the Earth's climate and external events such as large volcanic eruptions. However, these natural cycles cannot explain the full extent of the changes that the earth's climate has experienced since the beginning of the industrial revolution in the 1800s [7]. Instead, the primary driving force behind the significant shifts stem from human activities, particularly the emission of greenhouse gases, with CO_2 standing out as a key contributor [7].

Over the past two centuries, there has been a substantial increase in the atmospheric concentration of CO_2, recently reaching approximately 420 ppm [20]. Figure 1 shows the concentration of CO_2 in the atmosphere based on direct monthly measurements between 1958 and 2023 [20]. The annual cycles shown in the graph are the seasonal cycles of photosynthesis in the north hemisphere, where plants utilise CO_2 for their growth [20]. The overall increase over the years is predominantly attributed to emissions stemming from the combustion of fossil fuels. Electricity production accounts for around 40% of all CO_2 emitted by humans in 2022 [21]. This is then followed by industry and transport which account for 26% and 23% of human caused CO_2 emissions respectively [21].



Source: climate.nasa.gov

Figure 1 - Carbon dioxide levels in the atmosphere, ppm, 1958-2023 [1]

3.2 Carbon Capture

Carbon capture, also called CO_2 capture, is the removal of CO_2 from large scale sources of CO_2, such as power plants and even directly from ambient air. The CO_2 can then be either stored long term or utilised for industrial purposes. This section explains the various CO_2 capture technologies, and their advantages and disadvantages.

3.2.1 Various Forms of Carbon Capture

The primary forms of CO_2 capture are categorised into three primary categories: pre-combustion, oxyfuel combustion, and post-combustion. These methods mainly differ in the concentration of CO_2 in the gas stream from which it is removed, and the technologies employed.

Pre-combustion

Pre-combustion carbon capture involves removal of carbon from fossil fuels before combustion is completed [22]. The most widely used example is the gasification of solid fossil fuels such as coal, which involves partially oxidising coal with steam and oxygen to form synthesis gas. Synthesis gas, a valuable mixture of H_2 and carbon monoxide, can be further converted via the water-gas shift reaction to form a mixture of H_2 and CO_2. The CO_2 is removed from this mixture and the H_2 can then be combusted as a carbon free fuel. Alternatively, greener fuels such as biomass can replace coal in this process, enhancing the potential of this form of carbon capture for the energy transition.

Oxy-fuel Combustion

Oxy-fuel combustion is a particularly interesting form of carbon capture which involves the combustion of fossil fuels in nearly pure oxygen [23]. This oxygen rich environment results in the flue gases containing predominantly CO_2 and water. The significantly higher CO_2 concentration in the flue gases, compared to conventional combustion, facilitates more straightforward CO_2 capture [23]. However, the process of separating oxygen from the air to form the oxygen rich combustion environment is energy intensive, reducing the overall energy savings achieved [23]. Additionally, implementing this technique requires some modifications to power plants and other related processes, limiting their adaptability for retrofitting into existing plants.

Post-combustion

Carbon Capture directly from exhaust gases of industrial plants is already being used in industry [24]. The relatively low concentration of CO_2 in the flue gases in this process, 5-15 % depending on the type of power plant used, introduces a technical challenge for carbon capture. It increases the energy associated with the carbon capture process, with estimates of around 3 MJ/kg of CO_2 captured [25]. Despite the energy challenge, the advantage of this approach is that it only requires treatment of the flue gases, eliminating the need for modifications to the core industrial processes [23].

3.2.2 Carbon Capture Technologies

This section will discuss different carbon capture technologies. The most commonly used methods include membrane separation, adsorption, and absorption. Other methods are possible and will continue to be a focus of research, however these are considered to be the most mature processes at the moment.

Membrane separation is considered a promising technology for carbon capture. This separation technique relies on the principle that the membrane selectively allows CO_2 through over other gases. This separation technique can be used for both pre-combustion and post-combustion carbon captures. For post-combustion carbon capture, which mainly targets the removal of CO_2 from nitrogen, this system is expected to offer economic and energy savings compared to other techniques once it is mature [23]. However, it suffers the drawback of membranes being relatively easy to damage during operation and poor separation quality for CO_2 [23], [26].

Adsorption is a process where an adsorbate adheres to the surface of an adsorbent, and this interaction can be either physical or chemical. For CO_2 capture the common adsorbents used are zeolites, metal oxides, or an amine functionalised solid. These materials are then regenerated by pressure or temperature swing systems. However, the system has relatively low capture capacity in comparison to chemical absorption using materials such as amines [23].

Carbon capture using absorbing materials is the most technically mature process available and is already used in industrial applications. Some of most commonly used and researched materials for this process are aqueous amines, including Monoethanolamine (MEA) and Diethanolamine (DEA). These solvents are more selective towards CO_2 than to other gases present in flue gases or air, which means that they effectively remove the CO_2 from the gas stream. These solvents chemically absorb the CO_2 to form carbamates and various other chemicals. The reversibility of this reaction allows for the release of CO_2 and regeneration of the solvent, typically achieved through a temperature or pressure swing. However, the regeneration step poses significant challenges, demanding substantial energy input. The high temperatures involved in this process can also lead to solvent degradation, limiting both its lifespan and CO_2 absorption capacity. MEA is the industrial standard amine and is often used as a benchmark to compare the relative performance of other amines [17]. It is used primarily due to its relatively high solubility of CO_2, with good CO_2 carrying capacity per kilogram of solvent [17]. Additionally, it is relatively fast to absorb CO_2, increasing the efficiency of this step of the process [17].

In the process of carbon capture using aqueous amines, the captured CO_2 undergoes further utilization for industrial purposes, serving as a feedstock for the chemical industry or finding applications in the food industry. Alternatively, it can be directed towards long-term storage. However, the CO_2 must first be separated from the solvent, and subsequent processes are performed to prepare it for utilization or storage.

3.3 Carbon Capture and Utilisation

Once CO_2 is captured, it can be either stored for a long-term use known as Carbon Capture and Storage (CCS) or utilized as a feedstock for other processes known as Carbon Capture and Utilization (CCU). Long term CCS is considered as the approach which will play the biggest role in dealing with captured CO_2, with the IEA stating that it is unlikely that CCU will be able to provide large scale negative CO_2 emissions alone [11]. However, CCU is a particularly interesting route to deal with the captured CO_2 as it can turn the undesired waste of CO_2 into relatively valuable products. Currently, the major applications for captured CO_2 are for fertiliser production and enhanced oil recovery. Enhanced oil recovery involves injecting CO_2 into oil and gas reservoirs to extract more fossil fuels than feasible before. As the world increasingly seeks cleaner fuels and sustainable ways to synthesize chemicals, additional uses for captured CO_2 are gaining interest.

3.3.1 Catalytic Conversion

Catalytic conversion of CO_2 into more useful products can be done in several ways. Firstly, the Reverse Water Gas Shift (RWGS) reaction can be used to convert CO_2 into carbon monoxide. This carbon monoxide is relatively valuable for chemical synthesis as it can be utilised in the Fischer-Tropsch process as well as in other industries such as metal fabrication and the pharmaceutical industry. It is also possible and in many cases preferable to directly convert the captured CO_2 into longer chain hydrocarbons, including ethane and alcohols such as methanol. The main technical issues associated with this conversion to high value hydrocarbons is the general inertness of CO_2, the wide range of products produced in the reaction, and the production of lower value carbon monoxide. This is an area of active research to develop new catalysts and reactors in order to make this process more efficient and sustainable.

3.3.2 Electrochemical Conversion

Electrochemical conversion of CO_2 into useful products involves the reduction of the CO_2 into either carbon monoxide or other carbon containing species in an electrochemical cell. This has gained particular interest in the area of CCU as it can be operated at more ambient conditions than the catalytic route and can be easily integrated with renewable energy generation to power it. However, there remain some technical issues that are holding the process back from large scale implementation, including finding a suitable electrolyte, suppression of the Hydrogen Evolution Reaction (HER), and poor product distribution[3].

3.4 Deep Eutectic Solvents

Deep Eutectic Solvents (DES) are a class of solvents with similar properties to ionic liquids initially introduced by Abbott in 2003 [27]. They are formed by mixing a suitable Hydrogen Bond Donor (HBD) with a Hydrogen Bond Acceptor (HBA). When the appropriate chemicals are combined, the resulting mixture exhibits a significantly reduced melting point compared to its individual components. The combination of choline chloride and urea with molar ratio of 1 to 2 was the first of these DESs formed, with a melting point of 12 °C, compared to a melting point of 302 °C and 133 °C for urea and choline chloride, respectively [27].

This class of solvents is considered to be a good alternative to other solvent classes such as ionic liquids [28]. DESs have several key advantages, including better economic performance, ease of preparation, biodegradability, high thermal stability, and lower toxicity [29]. These characteristics make it possible to produce DES with high purity and at low costs on a relatively large scale for various industrial uses. In addition, DES can also be formed from amines, enhancing their carbon capture potential.

DES are categorised into four classifications based on the species used in their preparation, these are shown in Table 1 [30]. Both type I and II involve a combination of a quaternary ammonium salt and a metal chloride. Type III DES generally consist of a mixture of a quaternary ammonium salt with a HBD which is generally a small organic molecule [30]. The most common ammonium salt for type III DES is choline chloride as it is considered to be relatively sustainable and low in costs [30]. Choline chloride is most commonly combined with molecules such as urea or ethylene glycol, which are considered to also be relatively safe to handle.

Table 1 – Classes of DES [30] .

Types of DES	General Formula	Terms
Type I	$Cat^{+}MCL_{X}$	M = Zn, Sn, Fe, Al, Ga
Type II	$Cat^{+}MCL_{X}yH_2O$	M = Cr, Co, Cu, Ni, Fe
Type III	$Cat^{+} X^{-} RZ$	Z = $CONH_2$, COOH, OH
Type IV	$MCL_{x}RZ$	M = Al, Zn Z= $CONH_2$

3.5 Choline Chloride

Choline chloride is an organic quaternary ammonium salt with the chemical formula $[(CH_3)_3NCH_2CH_2OH]^{+}Cl^{-}$. The structure of choline chloride is shown in Figure 2 below. It is relatively inexpensive to manufacture, nontoxic, and biodegradable. It is currently produced in large quantities mainly as an additive in animal feed. For this thesis project, the focus is on choline chloride's ability to form a DES with various HBDs. These DES exhibit good conductivity and relatively high solubility of CO_2, making them well-suited for the applications required in this work. Furthermore, it has been widely reported in the literature that choline chloride can form DES with various amines, suggesting that a DES can be created and coupled with an amine to enhance its CO_2 solubility.

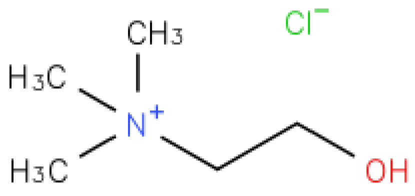


Figure 2 - Structure of choline chloride [2]

4 Literature Review

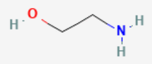
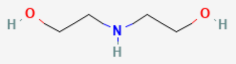
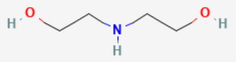
This section covers a broad review of the literature surrounding the subject of the integrated system of carbon capture and electrochemical reduction of CO_2 using DES coupled with amines. Firstly, the current state of carbon capture is reviewed, specifically looking at how the industry standard aqueous amine solvents perform this role, and the drawbacks associated with this process. Various aqueous amine solvents used in industry are subsequently reviewed. Next, the recently proposed integrated system of carbon capture and electrochemical reduction is examined, specifically covering how traditional capture mediums can be used. Deep eutectic solvents and their use for carbon capture are then reviewed, along with how these can be coupled with amines to enhance their carbon capture potential. The literature of using these DES coupled with amines for both carbon capture and electrochemical reduction are reviewed, and from this a suitable solvent chosen for the experimental work in this project. Lastly, the stability of the system in question is explored and literature on how to increase the lifetime of the system using pulsed electrolysis is examined to determine the optimal process conditions to be used in the experimental section of this project.

4.1 Aqueous Amine Based Carbon Capture

Post combustion carbon capture generally involves the use of absorbing materials to remove CO_2 from the flue gases of combustion or industrial processes [26]. Post-combustion carbon capture has the large advantage of a high concentration of CO_2 in exhaust gases, 30,000 ppm, compared to ambient air at 421 ppm [31]. Currently, the primary materials used in industrial absorption-based carbon capture are aqueous amines, such as MEA [26]. At present this is the most economical way to perform absorption-based carbon capture and is already in use on an industrial scale [32]. However, this method requires a relatively large amount of energy to implement and only separates around 85-90% of the carbon dioxide present in the exhaust gases, meaning that a relatively large amount of CO_2 is still emitted into the atmosphere [33].

Amines come in three main types depending on their structure: primary, secondary, and tertiary. This classification is based on the number of carbon chains linked to the central nitrogen atom. The different classes of amines and examples of their structures are shown below in Table 2. The structure of amines has an important influence on how they interact with CO_2 and the strength of this interaction [34]. The general trend for reactivity is that primary amines are the most reactive, followed by secondary and then tertiary amines [34]. MEA, a primary amine, is one of the most widely used due to its high absorption rate and loading capacity of CO_2, as well as its relatively good resistance to degradation compared to alternative capture mediums [15].

Table 2 - Types of amines and their structures [35], [36], [37]

Type	Structure
Primary	
Secondary	
Tertiary	

The system of carbon capture using aqueous amines works in several steps as shown in Figure 3. Firstly, the gas stream containing carbon dioxide is contacted with the aqueous amine solution in an absorbing tower [26]. The amine solvent is highly selective towards CO_2 over other gases, so the solvent leaves the absorbing tower rich in CO_2 and the exhaust gases lean in CO_2. This CO_2 rich solvent is then transferred to a stripping column [26]. Here it is regenerated to remove the CO_2, using temperature or pressure swing desorption. The regenerated amine solvent is then recycled back into the absorbing tower where it is able to capture more CO_2. The final step is then to send the released high purity CO_2 stream to be compressed for eventual use or storage. Some solvent make up is required as a small amount of solvent is lost during the regeneration step and the solvent starts to degrade due to the operating conditions of the system. The most energy intensive part of this process is the temperature swing desorption process and compression steps, accounting for 90% of the total operating costs [14].

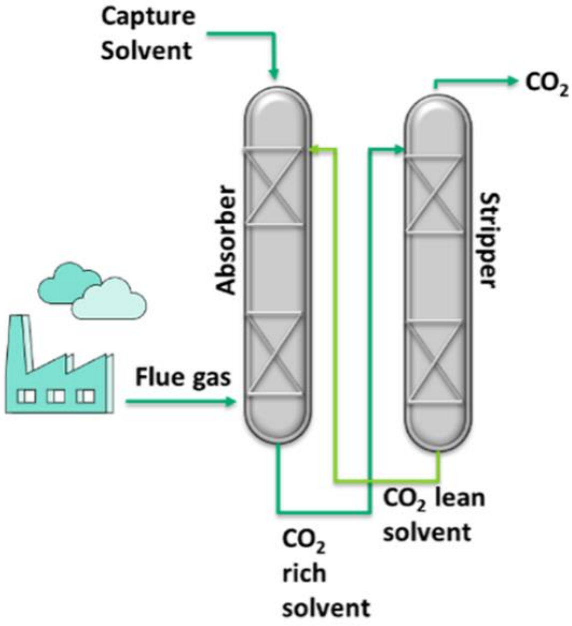


Figure 3 - Diagram of the standard carbon capture process [3]

The mechanism by which the absorption into the amine solution occurs is complex and depends on the type of amine used [26]. For primary and secondary amines the most widely accepted mechanism is via the formation of zwitterions as shown below [38]. This process involves the initial formation of zwitterions, which are formed by reacting the primary or secondary amine with CO_2. This zwitterion is then immediately neutralised by a base such as the amine or hydroxide ions [38]. The simplified chemical equations for the reactions are shown in Equations 1 and 2, generalised for the primary amine of MEA [14].

$$CO_2 + MEA \rightleftharpoons MEACOOH \qquad \text{(eq. 1)}$$

$$MEACOOH + MEA \rightleftharpoons RNHCOO^- + RNH_3^+ \qquad \text{(eq. 2)}$$

In an investigation into the mechanism by which CO_2 is captured by MEA it was found that the capture happens in two steps [38]. Firstly, the CO_2 loading in the MEA solution increases rapidly along with an increase in temperature and a decrease in pH. The second stage then proceeds with a much slower increase in the CO_2 loading of the solution as it becomes more saturated. The temperature then decreases, along with a slower decrease in the pH. The first stage accounts for nearly 80% of all the CO_2 absorbed in the process.

4.1.1 Issues with Amine Based Carbon Capture

There are several key technical issues with the traditional MEA based process that limit the use of this technology on a more widespread basis. Firstly, the loss of the solvent, MEA, from the system through degradation, vaporisation, and other routes presents an issue that has, according to literature, yet to be fully solved [26], [32]. This is not only an economic consideration but also an environmental and safety concern, as MEA is volatile and toxic [37]. While traps can be added to reduce the amount of amine lost into the atmosphere, there is still a concern about amines in aerosol form evading these traps [39]. Additionally, the degradation of amines is also another major concern for this process, particularly in this standard process set-up in which the stripping column used for amine regeneration is operating at relatively high temperatures. These elevated temperatures lead to amine degradation, including the formation of dimers and long amine chains [32]. Additionally, the amine solvent can be easily poisoned by both nitrogen oxides and sulphur oxides, both of which are commonly found in the flue gases from which the carbon dioxide is captured [32]. Corrosion is also a major issue in amine-based systems, particularly for MEA [26]. MEA is known to cause corrosion issues for process equipment, meaning that corrosion inhibitors or lower concentrations of MEA need to be used [26].

Overall, the biggest drawback of this process, and the focus of a large amount of research according to the literature, is the energy intensive nature of the process. As the regeneration of the solvent is done via a temperature or pressure swing it takes a lot of energy, this is particularly important for MEA as it has a relatively high heat of adsorption compared to other amines [40]. Additionally, the compression of the CO_2 product also requires large amounts of energy to be able to transport it using pipelines or for storage on site. This high energy requirement reduces the efficiency of the process and its ability to be widely used.

4.1.2 Comparison of Monoethanolamine to Other Amines

One proposed method to reduce the technical issues surrounding carbon capture using amines is the use of alternative amines, such as Diethanolamine (DEA). These alternative amines are known to be capable of CO_2 capture in similar ways to the standard MEA. A review by Li et al collected information on the species formed during the absorption of CO_2 by MEA, DEA, and MDEA [4]. The species and their concentrations with respect to the amount of CO2 loaded into them is shown below. Figure 4 shows that MEA and DEA have very similar reactions and the general trend of the concentrations of each species is similar. However, MDEA, shows a different trend in some of the key species, this is due to the dominance of bicarbonate formation in this amine [4].

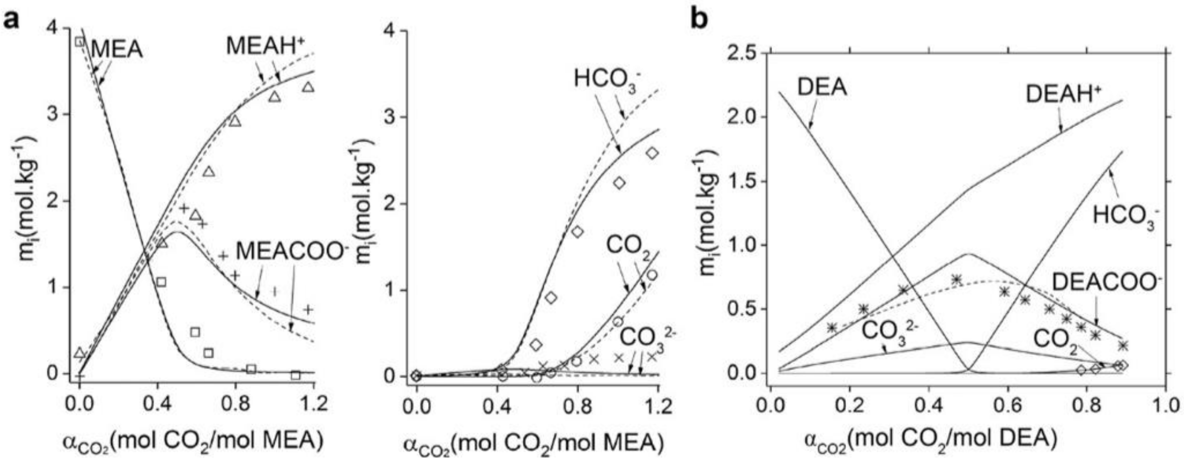


Figure 4 - Concentration of various species present during the absorption of CO2 into (a) MEA and (b) DEA [4]

In addition to these differences in the chemical reactions and the concentration of species during the reaction there is a difference in the energy required to regenerate these amines [40]. As amine regeneration is one of the largest costs associated with CO_2 capture, finding an amine with a lower regeneration energy is a key part to the process viability. This regeneration process makes up a large proportion of the energy required for carbon capture and can range from 2-4 MJ of energy per kg of carbon dioxide captured [41]. Studies have shown that DEA potentially has lower energy requirements for the regeneration process due to the lower heat of absorption [40]. Also, corrosion caused by aqueous amines is a key concern for the CO_2 capture process and limits the concentration of amines that is able to be used in these systems. Corrosion by amines is only considered to be a major issue after they react with CO_2 or when they have formed degradation products. Generally, MEA is only used at around 30% by weight in the capture medium due to these corrosion and other issues[34]. Fleury found that DEA is half as corrosive as MEA, meaning that it can be used at higher concentrations before it causes issues with the process equipment [42]. Additionally, DEA has lower levels of reactivity with sulphur containing compounds which are present in the flue gases of industrial processes, meaning that there is less poisoning and degradation of the capture medium [43].

Lastly, the thermal stability varies between the types of amines. It is generally considered that tertiary amines are the most thermally stable while primary amines are the least [44]. Thermal degradation is reported by Rochelle to form products that are more volatile and less able to absorb CO_2 than the amine [43]. This means that thermal degradation needs to be avoided for environmental reasons and in order to keep the solvent usable for as long as possible. However, as the efficiency of CO_2 capture is inversely related to this thermal stability, a compromise must be made between the CO_2 capture and the lifetime of the solvent.

4.2 Carbon Capture and Use

As previously stated, there is two options of what to do with the captured CO_2 in this process, it can be placed into long term storage, or it can be utilised. Long term storage can be achieved through placing the CO_2 into underground depleted oil reservoirs or through mineral carbonation. According to the IEA this form is likely to deal with the vast majority of captured CO_2 in the future and is likely to be the best way to achieve large scale negative carbon emissions [12]. This technology was used for the first time on a large scale by Equinor in the Sleipner project starting in 1996 [45]. However, utilising the captured CO_2 is seen by the IEA and others as providing a pathway to produce synthetic fuels and other chemicals in a more environmentally friendly way.

4.2.1 Current State of Carbon Capture and Use

CCU was first used in the 1960s; when carbon dioxide removed from natural gas streams was used for enhanced oil recovery [45]. This is a physical utilisation of carbon dioxide and involves injecting carbon dioxide into mature oil fields to allow the continued extraction of oil. This remains one of the largest uses for captured carbon dioxide today but utilising it instead to produce chemicals and fuels is considered a viable alternative which would help mitigate climate change. This chemical utilisation of carbon dioxide is the conversion of the captured carbon dioxide into useful chemicals, primarily the production of carbon monoxide, formate, or even longer chain hydrocarbons and alcohols [12]. However, this remains a relatively niche technology, with 230 Mt of CO_2 per year utilised, which still includes a large amount used solely for natural gas processing [11]. This relatively small scale of utilisation of carbon dioxide is due to many factors, with the costs and energy required to capture and convert the CO_2 into useful products being some of the major issues.

One of the most promising routes to utilising CO_2 for chemical use is the electrochemical reduction to CO or long chain hydrocarbons. This is done in an electrochemical cell in which an electrolyte suitable to carry the CO_2 through the system is used, and a metal such as silver or copper is used as the cathode. The choice of material for the cathode has a large influence on the products formed during this reaction. At the cathode generally there are two main competing reactions, the CO_2 reduction and the HER. It is often the case that the HER is undesirable and should be suppressed, however some level of H_2 production is always inevitable. At the anode the reaction is the Oxygen Evolution Reaction (OER) [46].

4.2.2 Integrated System of Capture and Electrochemical Reduction Using Conventional Amine Solvents

To overcome the high energy costs associated with capture and conversion of CO_2, which largely come from the solvent regeneration step, an alternative system has been proposed [14]. This new system is an integrated system of capture and electrochemical conversion of CO_2 as shown in Figure 5. This coupled system also uses the capture material as the electrolyte material, and it has been shown to reduce the costs associated with carbon capture in certain conditions. Using common carbon capture solvents such as MEA is possible for this system but has some inherent drawbacks associated with it [14]. This use of the same material for both the capture and electrochemical conversion steps is comparatively unstudied in literature as this is a relatively new innovation [14]. A diagram of how this integrated system works is shown below in Figure 5 [3].

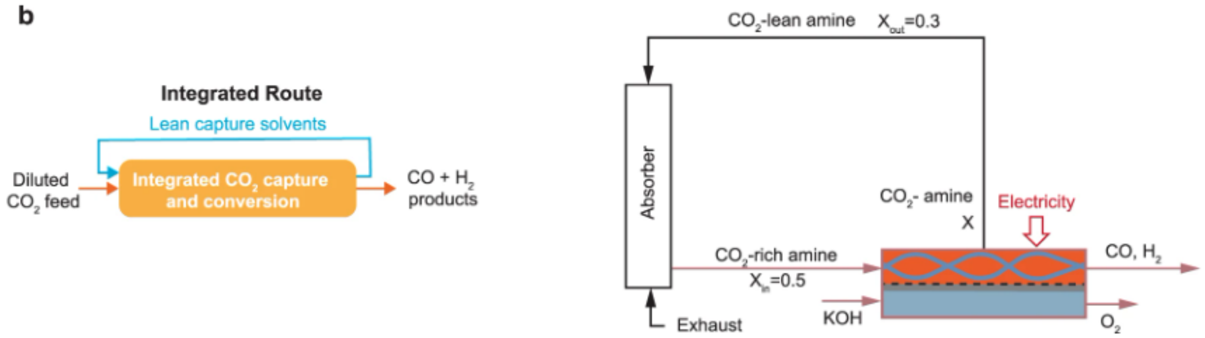


Figure 5 - Diagram of integrated carbon capture and electrochemical conversion [5]

For MEA, the benchmark solvent for carbon dioxide capture, Chen proposes that there are a series of complex reactions occurring at the electrode surface [14]. Free CO_2 is considered to be the most active reactant in this process [14]. Firstly, the CO_2 adsorbs onto the metal surface at vacancies indicated with an asterisk, and this is then converted to a carbon dioxide radical anion [14]. This series of reactions are shown in Equations 3 and 4 [14].

$$CO_2 + * \rightleftharpoons CO_2^* \qquad \text{(eq. 3)}$$

$$CO_2^* + e^- \rightleftharpoons CO_2^{-*} \qquad \text{(eq. 4)}$$

This free radical anion of CO_2 is then converted into either CO or formate ions. Chen notes that with appropriate catalysts and conditions more valuable alcohols and hydrocarbons could instead be directly formed [14]. They do not however detail which catalysts or conditions would be required for this to happen. Chen found in 2017 that using MEA 30 % (w/w) aqueous solution with silver electrodes leads to a faradaic efficiency of only 6.1 % when using relatively high potentials of -1.1V [14]. In this scenario the predominant product is H_2 with a faradaic efficiency of 93% [14]. The faradaic efficiency of carbon monoxide production can be increased up to 12% using silver electrodes, if these electrodes are porous. This however leads to most of the CO_2 being unconverted, leading to potentially low solvent regeneration and low process efficiencies. Chen found that the HER needs to be inhibited in order for this process to be as efficient as possible [14]. They suggested that including surfactants and using porous electrodes would inhibit the HER and lead to higher faradaic efficiencies for the CO_2 reduction [14].

Perez-Gallent conducted experiments in this integrated system using 2-amino-2-methyl-1-propanol (AMP) and propylene carbonate (PC) as the electrolyte [3]. This follows a similar reaction pathway to the one that Chen found, as the solution approaches the electrode the carbon dioxide is liberated from the complexes [14]. This is achieved through elevated temperatures which are easily reached due to the ohmic losses associated with the electrochemical process occurring. Perez-Gallent also investigated the conversion and liberation of carbon dioxide from the electrolyte [3]. The study found that running the electrochemical conversion at 15 °C leads to very poor liberation of carbon dioxide from the solution, with the greatest liberation happening at 75 °C. After five hours of operating their system, the greatest percentage conversion of carbon dioxide was found to be around 30 % and this was at 45 °C. This is due to the experiment being run in an open system, meaning that the excess carbon dioxide liberated at higher temperatures which cannot be converted is lost out of the system. This is a limitation of experimental set up and presents problems with fully analysing the effectiveness of the system.

A further issue with the electrochemical reduction of carbon dioxide in MEA solutions is that free carbon dioxide is being utilised instead of the carbon dioxide in the complex. This means that the majority of the carbon dioxide is not being reduced, and therefore the MEA is not being regenerated efficiently. Chen gives several suggestions to overcome this issue including using different amines which have weaker carbon dioxide binding energies, so that the carbon dioxide can more easily dissociate from the complex [14]. Chen however does not suggest the use of different solvent classes altogether, instead preferring to stay with the industrial standard of aqueous amines. One possible alternative amine is DEA, as this has a lower strength of bonding associated with CO_2 adsorption than MEA.

The literature surrounding the use of traditional solvents in this integrated process points towards a need for further research into new solvents that are more suitable. One class of solvent that can be used are DES, which have several distinct advantages compared to traditional amines, and can even be coupled with amines to have greater carbon capture characteristics, as well as better properties for the electrochemical conversion step. The literature points towards using an amine in this system, possibly in conjunction with a new solvent class that more easily dissociates from the captured CO_2. To be viable for this process any new solvent will be examined against the benchmark of amine-based solvents as these are the current industry standard, looking specifically at aqueous MEA. The most important characteristics for the carbon capture role are the solvents' ability to quickly absorb and desorb the carbon dioxide, high loading capacity of carbon dioxide, low solvent costs, and solvent tolerance to contaminants.

4.3 Deep Eutectic Solvents and Their Properties

Utilising different solvents in this integrated system is one way to increase the overall efficiency of the system. Trivedi found that ionic liquids have been investigated, particularly amine functionalised ionic liquids [17]. These have good CO_2 uptake qualities. However, Trivedi states that there are still unresolved issues with ionic liquids, namely the high costs associated with synthesising these solvents, making them difficult to use on large scales [17]. Instead, Trivedi and others have proposed using DES for CO_2 capture [17]. Deep Eutectic Solvents (DES) are a class of liquids that were first described by Abott in 2003. These DES have similar properties to ionic liquids but are considered to be 'greener' and more affordable [24], [27]. They maintain the advantages of ionic liquids, being easy to tune and customise as required, but are non-toxic, biodegradable, and relatively easy to prepare. These solvents are formed by mixing a HBD and a HBA together, which then forms a mixture with a much lower melting point than the constituents of the mixture. The first DES were created from a mixture of choline chloride and different forms of urea by Abbott in 2003 [27].

It has been well established that MEA is able to form a DES with an appropriate HBA. In this DES MEA behaves as the hydrogen bond donor [47]. For this purpose, choline chloride has been proposed as a suitable HBA due to its relatively safety and low costs. Mixing amines with a DES is an active area of research in order to increase the CO_2 solubility of the mixture. It has been shown that a mixture of urea - choline chloride and MEA has a greater solubility than the DES without the MEA [48]. The advantage of forming DES with the amines traditionally used for carbon capture is generally higher solubility of CO_2 than if a standard DES was used instead. However, this DES suffers from very high viscosity and therefore low electrical conductivity. This leads to issues with the electrochemical conversion as it leads to high ohmic losses resulting in poor efficiency of the system. Other amines that are commonly used for carbon capture have also been reported to be able to form DES with choline chloride, such as DEA and MDEA. However, these have not been as extensively researched compared to MEA, however these alternatives will also be explored in the next section.

In order to be a viable solvent and electrolyte for this system the solvent needs to have certain key characteristics. It needs to have a high CO_2 loading capacity, in order to be sufficiently good at the CO_2 capture step. To act as a viable electrolyte the chosen DES needs to have good electrical conductivity and low viscosity, in addition to this it needs to be stable in the conditions that will be present in the electrochemical cell. To limit the size of this review two different amines, MEA and DEA, and two different DES, Choline chloride - ethylene glycol and choline chloride – urea, were selected to be analysed.

4.3.1 Electrical Conductivity and Viscosity

Viscosity is a key parameter for any fluid in chemical process, particularly when acting as an electrolyte, as electrical conductivity is normally inversely proportional to viscosity. Additionally, as the system will eventually act as a flow system the viscosity is a key parameter that needs controlling. It is found that for a mixture of MEA, ethylene glycol, and choline chloride the viscosity of the solution with fixed mole fractions of MEA decreases with an increase in ethylene glycol mole fraction. Additionally, while the mole fractions of MEA and ethylene glycol are kept in a constant ratio, it is found in literature that an increase in choline chloride causes an increase in viscosity. Kazarina also found that the viscosity of this mixture has a strong dependence on temperature, with an increase in temperature causing a sharp decrease in viscosity [49]. It has been found that particularly when the solution is loaded with CO_2 , as it would be in the electrochemical cell, the viscosity is lowest when a mole ratio of 1:4 of choline chloride to ethylene glycol is used across all ranges of MEA concentrations[50]. It was also found that an increase in the amount of MEA in the solvent increases the viscosity of solution when it is rich in CO_2 [50].

Other amine DES mixtures are also possible in the context of this system, including choline chloride - urea as the DES and DEA as the amine. Using urea and choline chloride as the DES has shown to be possible for the CO_2 capture step of the process, however it is limited by the relatively high viscosity of the mixture making its use more difficult in this system [51]. The choline chloride - urea mixture has a viscosity of roughly ten times that of ethylene glycol and choline chloride, meaning that it is much harder to work with and has a lower electrical conductivity [52]. It is therefore not considered to be suitable for use in the integrated system as it would be too difficult to work with this solvent in the electrochemical step as well as in the system more generally.

4.3.2 Carbon Dioxide Loading Capacity

The CO2 solubility of various DES and amines are well described in literature . To be effective for this system the proposed solvents need to be able to absorb large amounts of CO_2 in a relatively small time. For amines it is well known in literature that MEA has the best performance for this compared to other aqueous amines. For aqueous amines at 30 wt % MEA has a high loading capacity of 0.426 moles of CO_2/mol amine compared to 0.404 moles of CO_2/mol of amine for DEA at 333 K. This higher loading capacity compared to DEA is seen at temperatures above 313 K, which is in the operational range of the proposed system. However, MEA does exhibit slower absorption of CO_2 compared to other amines such as DEA, meaning that there are drawbacks to the use of all amines and therefore a compromise is needed. For the mixture of MEA, ethylene glycol and choline chloride there is a clear increase in the CO_2 loading capacity per kilogram of the mixture with an increase in MEA concentration [49]. Additionally, the MEA-DES mixture shows a small decrease in CO_2 loading capacity when the ratio of choline chloride to ethylene glycol is increased while keeping the amount of MEA constant.

A solution of 1:4 choline chloride to ethylene glycol with 0.5 M MEA is considered to be the most interesting solvent to be studied in this project. The use of MEA is particularly interesting as it is already studied widely and is well understood for carbon capture uses. The choline chloride - ethylene glycol DES is likely the most viable candidate for the DES due to its relatively lower viscosity compared to other common DES. The exact ratio of the two components of the DES is chosen from literature data, and this 1:4 ratio is found to have the best compromise between CO_2 loading capacity and viscosity [50].

4.4 Pulsed Electrolysis

The system used for the electrochemical CO_2 reduction consists of three main components: the cathode, anode, and membrane. The anode, where the oxygen evolution reaction happens, and the membrane separating the two compartments are well described and considered to be stable over a long operational lifetime of tens of hours [53]. The cathode, in this case silver, is generally considered to be the most unstable part of this system [53]. Various routes of degradation can occur in the electrolysis cell including impurity deposition on the cathode, surface reconstruction, and electrode flooding [53].

4.4.1 Degradation Modes of Electrodes

The deposition of impurities on the electrode surface, known as electrode poisoning, has been reported in literature to cause deactivation of active sites used for CO_2 reduction and also enhance the HER [53]. These impurities can form from species present in the electrolyte, or products of the reaction that is occurring being irreversibly adsorbed by the cathode surface, resulting in large changes in the structure and active area of the electrode. Additionally, the electrode surface could go through structural changes during the electrochemical process which makes them less active for the CO_2 reduction reaction [53]. This structural change, called surface reconstruction, occurs when the active sites of the catalyst undergo a chemical or a physical change which causes a decrease in the selectivity or rate of CO_2 reduction. All these degradation modes are undesired and cause a reduction in activity and therefore either need to be avoided or reversed during operation. This can be done using different methods, such as chelating agents to suppress the deposition of impurities on the electrode surface or through pulse electrolysis [53].

4.4.2 Pulsed Electrolysis

Pulse electrolysis is one of the leading methods to reduce the effects of electrode degradation and can lead to more stable reaction conditions [53]. The standard operation of electrochemical reactions is at fixed operating conditions, either galvanostatically or potentiostatically, as this provides the simplest operation, and in ideal conditions continuous formation of the desired products. Pulse electrolysis on the other hand operates with changing potentials, with the potential of the cell changing throughout the process as shown in 6 [53]. Most studies into pulse electrolysis use simple square waveforms, while more complex waveforms such as sine or asymmetric waves have the potential to offer greater tunability of the electrode surface. The main process conditions that can be tuned in square waveform pulse electrolysis are the pulse times of the cathodic and anodic steps and the cathodic and anodic potentials themselves.

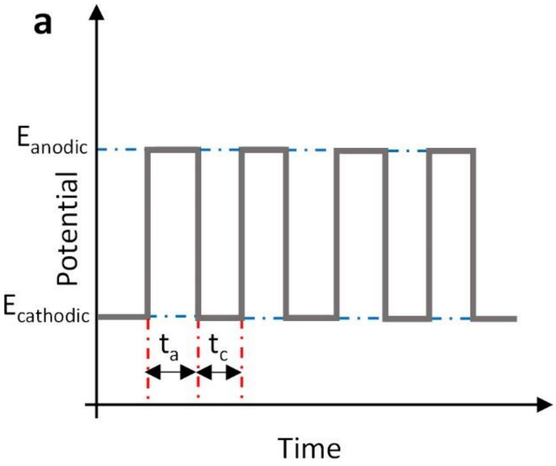


Figure 6 – Example of pulse electrolysis parameters for a square waveform [6]

It has been reported in literature that it is possible to reduce the impact of deposition of surface impurities by using pulse electrolysis. Yano found that pulse electrolysis, when using copper cathodes, successfully suppressed the deposition on the electrode of species that can lead to poisoning [54]. This was found to allow the system to remain at a stable Faradaic Efficiency (FE) for the desired products of methane and ethane for at least an hour [54]. It is possible that this effect is due to the oxidation of poisoning species during the anodic step in the pulse cycle, which means that the electrode surface is regenerated [54].

The process conditions for using pulse electrolysis for the system that will be used in this project are largely unknown. The reduction potential is unknown from literature and this needs to be determined before pulse electrolysis is performed in order to simplify the pulse electrolysis experiments. It is not known how long the system remains stable for, so the length of the cathodic pulse needs to be determined, along with the anodic potential and pulse time. It is important that the anodic potential is chosen so that it is still inside the stability window of the electrolyte to avoid unnecessary degradation, and that the anodic pulse time is chosen to be as short as possible to reduce the time that the system is not producing product. There is no literature information available for the electrolyte proposed in this project, specifically using MEA and choline chloride - ethylene glycol, and limited information on the use of silver working electrodes. Instead, the optimal cathodic pulse time, the time that the system is reducing CO_2, will be determined by experimental means. A range of anodic pulse times and potentials will be used to determine the optimal combination of these two parameters. These parameters are selected from literature of similar systems.

Additionally, further issues may be introduced by the pulse electrolysis step that will need to be monitored during the process. This includes possible electrode dissolution during the oxidation step of the process, this can lead to new degradation products and may introduce electrode failure in new ways [53]. Lastly, the effects of the cycling of potentials on the other parts of the cell such as the anode and membrane are not well understood or described in literature. If the cycles cause increased wear on the components and introduce further issues with the system that were not present before, this could reduce the lifetime and efficiency of the system.

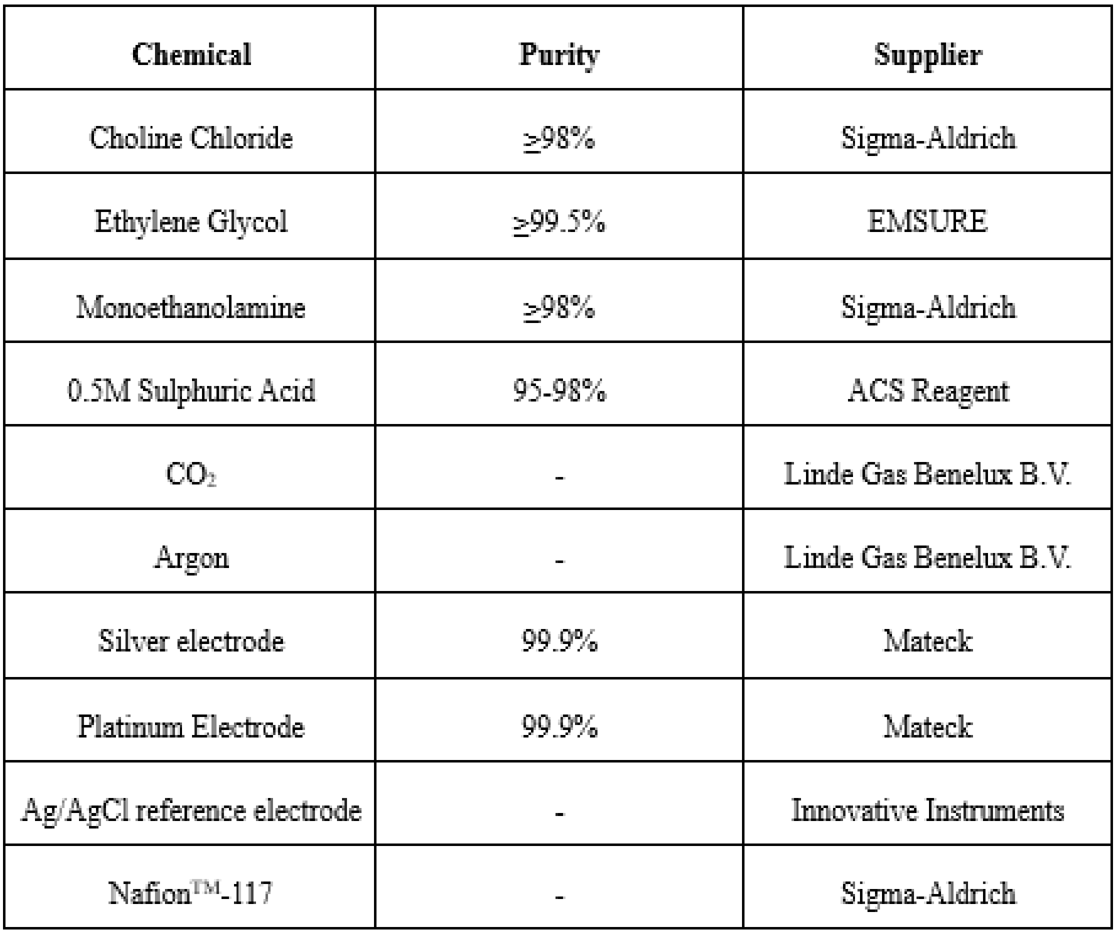
5 Methodology

This chapter covers the methodology of the experimental work completed for this research. Firstly, the preparation of the chemicals and materials, such as the electrolyte and electrodes, is detailed, which includes details of the suppliers and purities of materials used. Secondly, the set-up and operation of the electrochemical cell is explained, and the electrochemical techniques used are listed. Finally, a detailed overview of the experimental plan is provided.

5.1 Chemical and Material Preparation

The preparation of the materials is explained in this section, including preparation and loading of the electrolyte and preparation of electrodes. The various chemicals and materials used in this project are listed below in Table 3. The purity and the supplier of each of these is listed where appropriate.

Table 3 – Chemicals and materials used in this project.



Chemical	**Purity**	**Supplier**
Choline Chloride	≥98%	Sigma-Aldrich
Ethylene Glycol	≥99.5%	EMSURE
Monoethanolamine	≥98%	Sigma-Aldrich
0.5M Sulphuric Acid	95-98%	ACS Reagent
CO_2	-	Linde Gas Benelux B.V.
Argon	-	Linde Gas Benelux B.V.
Silver electrode	99.9%	Mateck
Platinum Electrode	99.9%	Mateck
Ag/AgCl reference electrode	-	Innovative Instruments
Nafion^{TM}-117	-	Sigma-Aldrich

The working electrodes used were silver (Ag) foils purchased from Mateck (1.0 x 25 x 25 mm 99.9% metal basis). To prepare these electrodes for use after they were received from the supplier, they were first sanded using silicon carbide sanding papers (from #80 to #2000). The electrodes were then subsequently polished to a mirror like finish using diamond suspensions and alumina pastes. Once polished the electrodes were placed in an ultrasonic bath to remove any lasting traces of the polishing solutions, and then rinsed using ultra-pure water and dried using an air stream. The counter electrode was platinum foil purchased from Mateck (1.0 x 25 x 25mm 99.99% metal basis). To remove any organic impurities deposited on the counter electrode during previous experiments, it was flame annealed before and after each experiment. No further preparation was conducted on the platinum counter electrode. Both the anode and cathode have a surface area in contact with the solutions of 1 cm^2, this means throughout the report that current (mA) and current density (mA/cm^2) are used interchangeably. A leak-free Ag/AgCl (1mm OD, LF-1, Innovative Instruments) electrode was used as the reference electrode, this was stored in 3 M KCl solution. The cation exchange membrane was Nafion^{TM} – 117 (thickness 0.007 inch, perfluorinated, Sigma-Aldrich) stored in ultrapure water, a new membrane was used for each experiment to avoid any leaks between the compartments.

Preparation of the solvent is one of the most important steps of the experimental process to ensure repeatable and accurate results. The details including exact amounts of each material added to the solvent mixture is provided in Appendix A. The choline chloride and ethylene glycol were mixed in a molar ratio of 1:4, this mixture was gently stirred at 80 $^{\circ}C$ for approximately 2 hours until it was clear and homogenous. The solution is then allowed to cool to room temperature and stored in a sealed container to avoid contamination. The final mixture was prepared by adding MEA into the choline chloride - ethylene glycol mixture, to make a solution of 0.5 M MEA. This was then mixed at room temperature to ensure that the solution was fully homogenous. This amine-DES mixture was then placed in a gas washing bottle through which pure CO_2 was passed for two days, until the mixture was viscous and light orange in colour. The exact amount of CO_2 loaded into the solution is unknown and it is assumed that it is saturated at the end of the loading period. Further analysis is possible to determine the loading of the solvent using barium chloride titrations and this is explained in subsequent sections. Due to the lack of knowledge about the amount of CO_2 being loaded into the solution it is important that all solution for the experiments is loaded at once. This helps to ensure that the solution used in each experiment is of uniform CO_2 concentration.

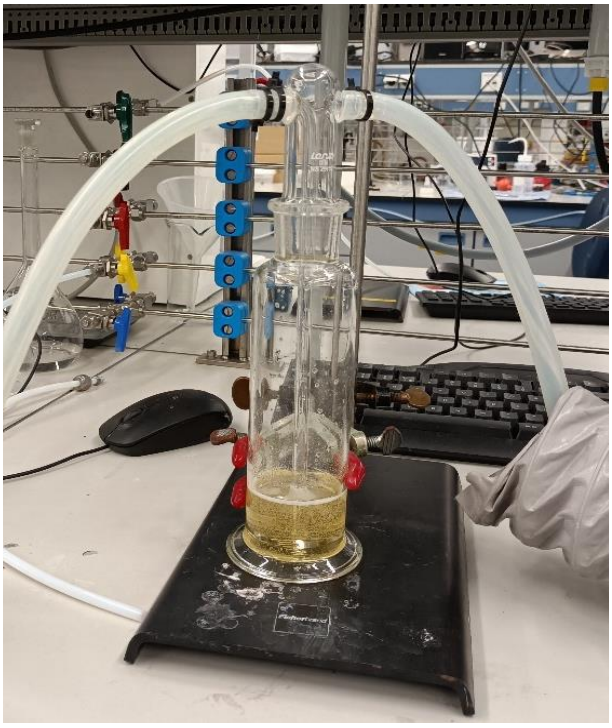


Figure 7 – Gas loading set-up, with the distinct yellow/orange colour of solution showing that it is loaded with CO_2.

5.2 H-Cell Configuration, Operation, and Analysis

The experiments investigating the electrochemical conversion steps are completed using a standard H-cell setup. The H-cell setup is ideal for this stage of development of a new electrochemical process as it is simple to use and setup, requiring only small amounts of solution, meaning it is relatively quick to reproduce experiments.

5.2.1 Standard H-Cell Setup

The H-cell used is a two-compartment cell with a cathode and anode compartment both with several ports available in order to place thermocouples, gas lines, and other equipment. Each compartment is approximately 2 ml in volume. The two compartments were separated by a membrane of Nafion-117, which selectively allows protons through, in order to allow the formation of carbamates for CO_2 reduction. For the Nafion-117 membrane it is important that the temperature of the cell is kept below 70 °C to avoid damaging the membrane. Before set-up of the cell commenced all components were rinsed with ultrapure water, including the cell itself, the electrodes, and the membrane. This cleaning is important to remove any impurities or substances from previous experiments that may still be present. The different parts of the cell were also thoroughly dried before assembly to stop any water being left in the cell.

The cathode compartment consists of the catholyte of the MEA, ethylene oxide, and choline chloride along with the working electrode of silver. The cathode compartment also consists of a reference electrode. The cathode compartment has an additional two gas pipes attached to it to allow for gas inflow, such as CO_2 to keep the catholyte saturated, and a gas pipe outlet at the top to allow for the products to enter the Gas Chromatograph (GC). It is important to allow the inflow of CO_2 for experiments in which CO_2 saturated solution is used to ensure that the electrolyte is not depleted. This helps to more accurately imitate industrial processes in which new electrolyte, saturated in CO_2, would be constantly flowing into the cathode. For the experiments in which CO_2 is purged into the bottom of the cathode compartment, it is important to include a one-way valve in order to stop catholyte loss from the cell.

The anode compartment consists of an anolyte of 0.5 M sulphuric acid and a counter electrode of platinum. The anode compartment was left to vent to the ambient air in the fume cupboard. Additionally, a thermocouple was present in the anode compartment, it was assumed due to the small nature of the cell that the two compartments are at the same temperatures. The thermocouple is wrapped in Teflon tape to reduce any contamination of the system by the metal present in the thermocouple wires. Previous experimental work had seen nickel present in the system after the experiments, which most likely came from the uncovered thermocouple wires.

The cell was then placed in a water bath, as shown in Figure 10, to allow it to reach the desired operating temperature through the use of conducting aluminium blocks. Insulating tape was then placed around the cell to reduce temperature fluctuations and to keep the cell at more uniform operating conditions. The cell was then connected to the potentiostat to allow for the voltage to the electrodes to be varied. Potentiostatic electrochemical impedance spectroscopy (PEIS) was then performed at both room temperature and the desired operating temperature of the system before the chronoamperometry (CA) is started. PEIS is then also completed the immediately after the CA is complete at the end of the experiment when the cell is still at operating temperature. The list of electrochemical techniques used in this project are detailed below. During operation the cathode compartment was always purged with either CO_2 or argon for two reasons. Firstly, the cell is very small so produces a relatively small amount of gas that would be too small for the equipment to work with. Secondly, for the experiments in which CO_2 loaded solution is used a CO_2 purge into the cell helps to keep the electrolyte saturated.

For all experiments the flow rate of the gas purge, of either argon or CO_2, is set at 15 ml/min. After the experiment is complete the catholyte and anolyte are removed and stored separately for later analysis. The volume of anolyte removed is often much smaller than the starting quantity due to losses to the atmosphere.

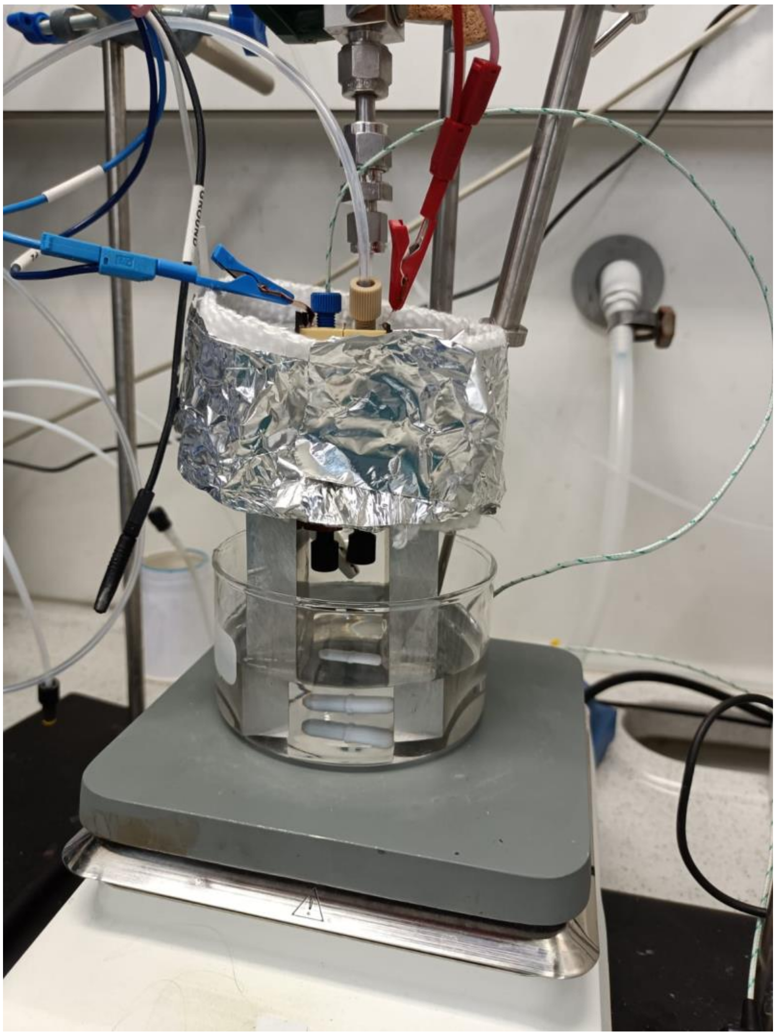


Figure 8 – The set-up of the H-cell with argon purging into the cathode compartment head space.

5.2.2. Electrochemical Techniques

Chronoamperometry

Chronoamperometry (CA) was used for the electrochemical experiments to apply a voltage across the system. This provides a square waveform to the working electrode, the silver cathode, and the current of the system is then measured. The potential is kept at a constant negative potential for the initial set of experiments into the system, and was then varied during the later stages of the experiments to examine the effects of pulse electrolysis. The current response is an interesting parameter as it allows for the Faradaic Efficiency (FE) of production of various components to be determined as well as giving an indication of how stable the system is. A large change in current during the operation of the cell would indicate that there are changes occurring to the components of the system, such as the electrolyte or the electrodes.

Open Circuit Voltammetry

One of the key electrochemical techniques used for this series of experiments is Open Circuit Voltammetry (OCV). This technique is used to determine if the reference electrode is performing in the expected way before the electrochemical reduction experiments are conducted. The OCV is the potential when there is no current flowing. For the electrodes used it is important that the OCV is stable during the test and is in the region of 10 mV of difference between them, showing that the reference electrode is performing as required.

5.2.3 Analytical techniques

Gas Chromatography

The gas product from the cathode compartment is analysed using an inline Gas Chromatograph (GC) (Compact GC$^{4.0}$, Global^{TM} Analyzer Solutions G.A.S) every 2 or 3 minutes for the duration of the experiment. The setup of the GC is with three channels, two thermal conductivity detector (TCD) channels and one flame ionisation detector (FID) channel. The GC was calibrated for the gas products of H_2, CO, methane, ethylene and ethane in ranges of 50 to 8000 ppm. This was done using calibration standards for the gases in CO_2 (Linde Gas Benelux B.V.). This allows for the amounts of H_2 and carbon monoxide to be determined, which in turn allows for the FE of the production of each of these to be determined. It was assumed for ease of experimental design and data analysis that the gas produced in the cell is detected almost instantaneously in the GC. This assumption simplifies the determination of the FE as the current at the detection time is then known. Lastly, it is assumed that there is no accumulation or loss of gases in the cathode compartment of the cell or in the lines, meaning that all gases flow through the gas lines equally and reach the GC for detection.

Faradaic Efficiency

The Faradaic Efficiency (FE) is a measure of the selectivity of each of the products formed during the CO_2 reduction reaction that is occurring in the cell [55]. It measures the ratio of the current used to produce a particular product to the total current in the cell [55]. To determine the FE of the production of each of the products first the relative peak area of each of the products is found from the GC data. This is then compared to the calibration data available for the GC, which is found using a known concentration of gases, and then the relative area is known for this concentration. This is repeated for a variety of different gas concentrations so that a correlation can be determined to find the concentration of the products from their relative areas.

For gaseous products this equation is converted to Equation 6 [55]. Where n_e is the number of moles of electrons that are needed to get 1 molecule of the product. The parts per million of the gaseous product in question is presented by x. The ambient temperature and pressure are given by T and P respectively. The faraday constant, gas constant and average current are given by F, R and I respectively.

$$FE\ (\%) = \frac{Q_{prod}}{Q_{total}} \times 100 \qquad \text{(eq. 5)}$$

$$FE_g = \frac{n_e \cdot x\ \cdot F \cdot flowrate\ \cdot P}{R \cdot T \cdot I} \qquad \text{(eq. 6)}$$

The sum of the FE of each of the components should be equal to 100%, however this may not always be the case due to issues with the experimental design and the lack of liquid phase analysis. There are likely to be some liquid products formed in the process, which require HPLC analysis to determine their concentrations. The samples from each experiment are saved for future analysis using HPLC. However, as the system is operating in a batch mode, with no flow of electrolyte through the system, it is not possible to determine when any liquid products formed during the experiment. This means that it will not be possible to determine accurately the FE of production of any liquid products for each time step of the experiment, however it is still of interest for future work to understand more clearly what liquid products do form. Additionally, issues with the flow metre measuring the flow of gas from the cell throughout the experiments means it possible that gas has leaked from the system undetected before entering the GC, which will affect the results.

Additionally, for the pulse electrolysis experiments there are several ways to try to account for the positive anodic pulses on the average current for each detection period of the GC. It is reasonable to assume that the entire current supplied is going to produce the known products and therefore that the total FE of the H_2 and CO combined is always 100%. This project instead used an average current for each of the pulses, and to do this the current for each cathodic pulse was allowed to settle for 30 seconds and then the average was taken for the remaining part of the pulse. This average current was then used as the current for the entire length of the cathodic pulse and the proceeding anodic pulse.

High Performance Liquid Chromatography

Samples of a selected number of experiments are set aside for use in High Performance Liquid Chromatography (HPLC) (Agilent 1260 Infinity, Agilent Technologies) to determine if there is any liquid product formation. For this analysis a small amount of solution, 5 μl, is injected into the two Aminex HPX-87 H columns (biorad) placed in series, heated up to 60 $^{\circ}$C. The HPLC machine was calibrated with standard aqueous solutions with concentrations of 0.1 mM to 50 mM for various liquid products, including oxalic acid, formate, acetic acid, ethylene glycol, ethanol and choline chloride.

6 Results

The results of the experiments performed in this project are presented in this chapter. Section 7.1 presents the results of the initial investigation into the system, including finding the optimal reduction potential and temperature. Section 7.2 then presents the results of the experiments in which pulse electrolysis was used, and how utilising it can successfully increase the stability of CO production. These two sections mainly examine the FE of the production of H_2 and CO, as well as the current response of the system. It should be noted for all experiments, issues with the equipment and the detection of H_2 can cause total FE of the system to increase slightly over 100%, which is not technically possible. This issue is considered to be small enough that the results are still valid as the general trend of the production is of most interest. For the experiments in which this issue was found it is noted alongside their results. All potentials referenced in this report are versus Ag/AgCl reference electrode. Each experiment is labelled with a corresponding experiment number for ease of finding data in the appendix.

6.1 Initial Investigation into System

In this section, the results of the initial investigation into the system are explored, which covers many of the initial parameters of the system that are not known from literature. This includes at which reduction potentials and temperatures there is the desired CO formation. Additionally, this section covers how stable the system is during operation, including the stability of the system's CO production and if the electrolyte is stable during operation at the conditions used.

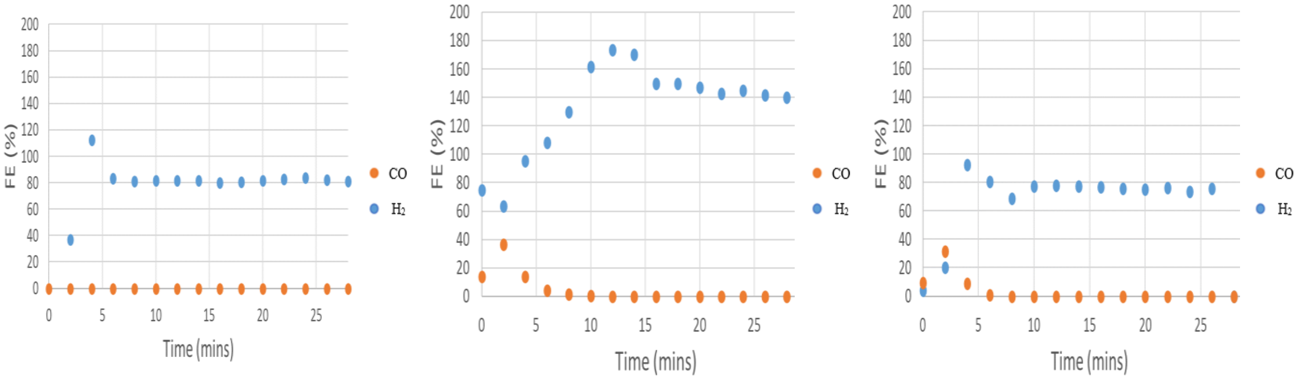
6.1.1 General System Stability and Proof of Concept

The first experiments for this project were designed to determine several parameters of the system, including if the system could produce the desired product of CO, if the system was stable during its operation, and at which voltages it operates optimally. This was done by setting up the cell in the standard method as described in Section 5, with a CO_2 loaded catholyte, purging CO_2 into the catholyte, and operating at 65 $^{\circ}$C. The cell then had a potential applied to it which was kept constant for each experiment. The details of the conditions used are provided in Table 4.

Table 4 – Experimental conditions initial proof of concept experiment.

Experimental condition	
Catholyte	0.5 M MEA in ChCl:EG 1:4 CO_2 loaded
Temperature	65 °C
CO_2 flow rate	15 ml/min
GC sampling time	3 min
Equipment	GC 6 (-1.5 V reduction vs. Ag/AgCl) / GC7 (-1.3 V and -1.7 V reduction vs. Ag/AgCl)

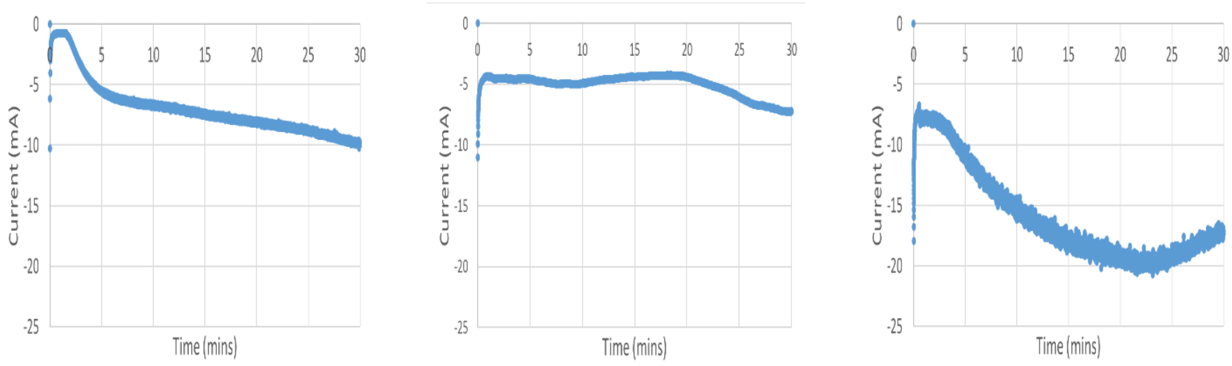
Figure 9 shows the FE of CO and H_2 production over the 30 minutes for experiments 1, 2 and 3 conducted at a constant reduction potential of -1.3 V, -1.5 V, or -1.7 V vs. Ag/AgCl reference electrode, respectively. For each of these potentials, the FE of H_2 production reaches a steady state between 5 and 10 minutes into the operation of the cell. For -1.3 V and -1.7 V vs. Ag/AgCl, this reaches a steady state of FE for H_2 production of 80%, for -1.5 V it is in the region of 140% due to the previously mentioned issues with the inlet gas streams being contaminated. The FE of CO production is much more unstable in comparison to the FE of H_2, decreasing from the start of the experiment and reaching zero within 10 minutes for reduction potentials of -1.5 V and -1.7 V. There is no CO production when using a reduction potential of -1.3 V, so this is not considered suitable for use, and it is not used in any further experiments. For -1.5 V and -1.7 V, they have very similar levels of FE for CO, with similar profiles across the entire operating time. Additionally, as the two experiments with potentials of -1.3 V and -1.7 V had a total FE of less than 100%, when the known products are taken into account it is possible additional products are being formed that are not detected using the current equipment. These could be either liquid products or gaseous products and further work is required to determine what is being formed. HPLC analysis is used on the liquid samples, however no further analysis of the gas products takes place as no gas samples are collected during the experiments.



(a) (b) (c)

Figure 9 - Faradaic efficiency of CO and H_2 for at 65 °C at a constant reduction potential vs. Ag/AgCl *of (a) -1.3 V (exp. 1) (b) -1.5 V (exp. 2) (c) -1.7V (exp. 3)*

The current response of the system for each of the three conditions used are shown in Figure 10. The current for -1.5 V shows a relatively stable profile for the first 20 minutes of operation of the cell, staying between 4.2 and 5 mA. After 20 minutes, the current starts to decrease, reaching 7.6 mA by the end of the experiment. The exact link between CO_2 reduction and the stability of the current is difficult to find from this result, as the end of the stable period of current does not align exactly with the end of CO production. For -1.3 V the current profile is unstable with steep decreases in current after the first two minutes of operation. Additionally, a similar profile is seen for -1.7 V with steep changes in current almost immediately from the start with minimal stability throughout operation of the cell.



(a) (b) (c)

Figure 10 – Current response at 65°C for a constant reduction potential v Ag/AgCl of (a) -1.3 V (exp.1) (b) -1.5 V (exp. 2) (c) -1.7 V (exp. 3)

The main results of this section are that it is possible to have the desired CO_2 reduction reaction running in this system but that it is unstable. The period of operation is limited to around 10 minutes for CO production, while the current is shown to not be able to be kept stable for operating longer than 20 minutes. It is also clear that utilising -1.3 V for the reduction potential is not suitable for CO production. While using -1.7 V is technically feasible to produce CO in this system it is clear from the current response that these conditions do not provide as stable an operation compared to -1.5 V. Therefore, the majority of experiments for this project are completed at a reduction potential of -1.5 V, with limited investigation of -1.7 V.

6.1.2 Electrolyte Decomposition

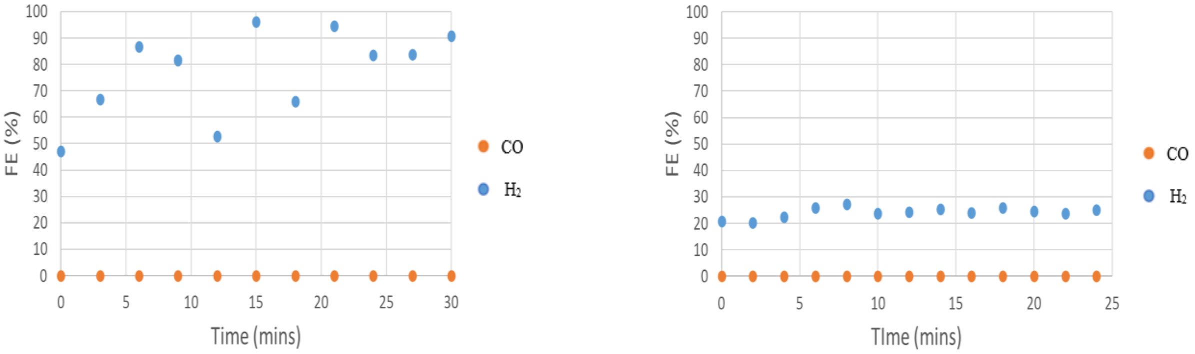
The next part of the experimental work was to determine the stability of the electrolyte and other components in operational conditions, which was done using a blank (not CO_2 loaded) solution of MEA, Ethylene Glycol, and Choline Chloride as the catholyte. This solution was prepared as described in Section 5, with 0.5M MEA and a ratio of 1:4 of Choline Chloride to Ethylene Glycol. The H-cell was set-up in the standard way, but with a purge of argon gas through the cathode head space at 15 ml/min, instead of CO_2. The overview of conditions used in this experiment are presented in Table 5. A reduction potential v Ag/AgCl of -1.5 V and -1.7 V were used as these are considered to be the most viable potentials for the system (exp. 5 and 6 respectively).

Table 5 – Conditions used for the electrolyte decomposition test.

Experimental condition	
Catholyte	0.5 M MEA in ChCl:EG 1:4 Not CO_2 loaded
Temperature	65 °C
Ar flow rate	15 ml/min
GC sampling time	3 min
Equipment	GC 6 (-1.5 V vs. Ag/AgCl reference electrode) / GC7 (-1.7 V vs. Ag/AgCl reference electrode)

The FE of the production of H_2 and CO over the course of the run time of the experiments are shown in Figure 11. There is no CO detected by the GC in either experiment the FE of CO production for both reduction potentials are zero. For a reduction potential of -1.5 V vs. Ag/AgCl, the FE of H_2 production is in the range of 50-95%, with an average of approximately

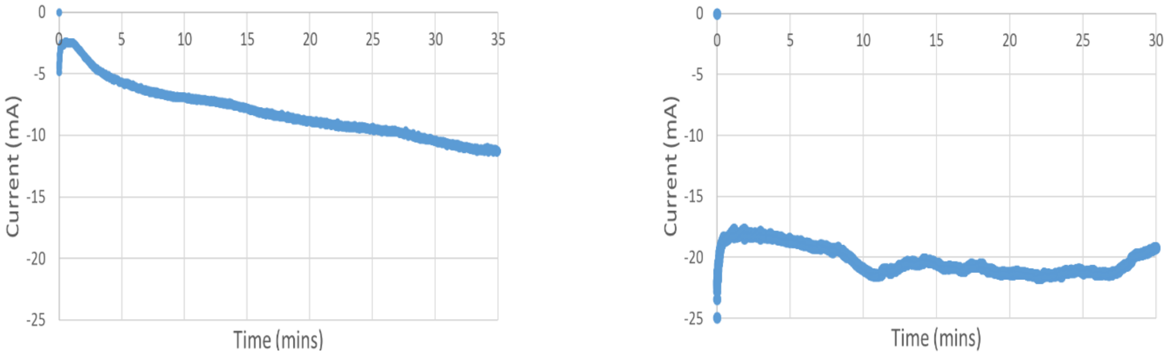
85%. For -1.7 V vs. Ag/AgCl, the FE of H_2 production is much lower at 20-30% which indicates that another reaction is occurring which is not being identified using the GC. Further analysis by HPLC is required to determine which liquid products might be being formed. The formation of additional unknown products when using -1.7 V is an indication that this condition might not be fully suitable for use as the electrolyte might be being degraded.



(a) (b)

Figure 11 - Faradaic efficiency of CO and H_2 *at 65 ˚C with blank solution at a constant reduction potential vs. Ag/AgCl of (a) -1.5 V (exp. 4) (b) -1.7 V (exp. 5)*

The current response of the system for these experiments is shown in Figure 12, and clearly shows a decrease in current over the course of the experiment for -1.5 V vs. Ag/AgCl reference electrode. The exact reason for the change in current over the course of the experiment is unknown but is likely due to changes in the electrode and the electrolyte during the course of the experiment. Further analysis using surface characterisation techniques is required to determine the exact cause. For -1.7 V vs. Ag/AgCl, the current is relatively stable, at around -22 mA, with smaller changes around this baseline than for -1.5 V vs. Ag/AgCl reference electrode.



(a) (b)

Figure 12 - Current response at 65 ˚C with blank solution at a constant reduction potential vs. Ag/AgCl of (a) -1.5 V (exp.4) (b) -1.7 V (exp. 5)

The key result from this section is that there is no CO detected when the blank catholyte solution is used with an argon purge for -1.5 V and -1.7 V as the reduction potential v Ag/AgCl . This means that in subsequent experiments with solutions that are loaded with CO_2 and purged with CO_2 that any CO detected is more likely to be from the CO_2 reduction reaction rather than electrolyte decomposition. It is also important to note that the current in this experiment is not stable, meaning that there is a change happening in the system which cannot be fully explained.

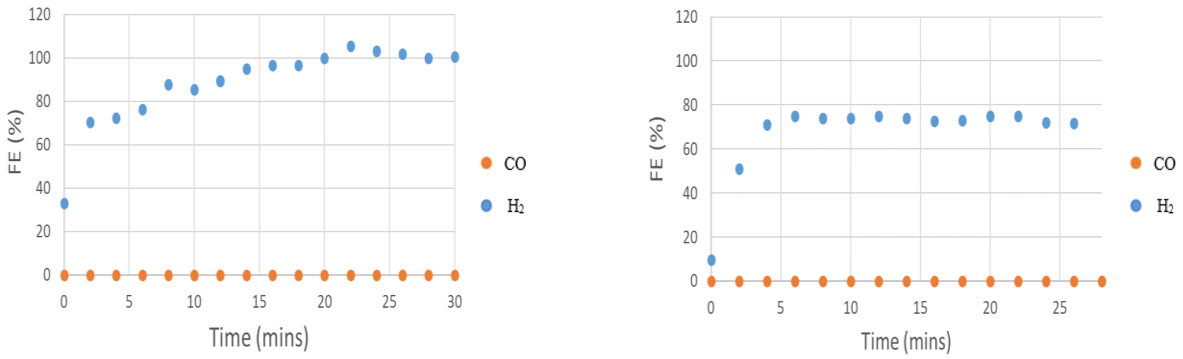
6.1.3 Optimal Temperature

Finding the temperature range in which the system can work is a key part of developing the system. All previous experiments have been completed at 65 °C, as the maximum operating temperature of the Nafion -117 membrane is approximately 70 °C. A lower temperature of 40 °C was chosen to see if this was suitable for use. A lower temperature would be more economical to run due to lower energy costs associated with the heating requirements. Reduction potentials v Ag/AgCl of -1.5 V and -1.7 V were used for this (exp. 6 and 7 respectively), the -1.3 V vs. Ag/AgCl potential was not considered due to lack of CO production at 65 °C. The cell is setup with a CO_2 loaded catholyte and a CO_2 purge into the cathode compartment at 15 ml/min.

Table 6 – Experimental conditions for optimal temperature experiments.

Experimental condition	
Catholyte	0.5 M MEA in ChCl:EG 1:4 CO_2 loaded
Temperature	40 °C
CO_2 flow rate	15 ml/min
GC sampling time	2 min
Equipment	GC 7

Figure 13 shows the FE of H_2 and CO production for these experiments and clearly indicates that there is no production of CO and relatively high amounts of H_2 being produced for both reduction potentials. This means that operating the cell at 40 °C is not considered to be viable in this current set-up, therefore all further experiments were completed at 65 °C. The FE of H_2 production for -1.5 V being above 100 % is an experimental error due to the impurities in the inlet gas line to the cell. The reason for lower than 100 % total FE for -1.7 V is most likely due to other products being formed that are also not detected by the GC either in the gas phase or liquid phase.



(a) (b)

Figure 13 - FE of CO and H_2 production at 40°C for reduction potentials vs. Ag/AgCl of (a) -1.5 V (exp. 6) (b) -1.7 V (exp. 7).

6.2 Pulsed Electrolysis

It is clear from Section 6.1 that there is some level of instability in the system during the electrochemical CO_2 reduction, which can be seen from the short time in which CO is produced and by the changes in the current throughout the experiments. From literature it is suggested that this is likely to be from changes to the cathode or the electrolyte [6]. This section of the results seeks to cover the effect of introducing pulse electrolysis on the system, in the form of short anodic pulses followed by longer cathodic pulses.

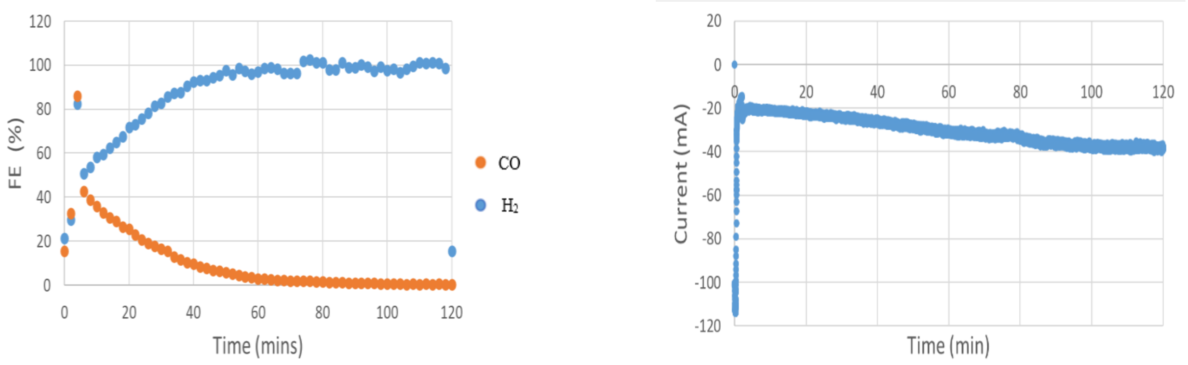
Pulse electrolysis is seen as one of the most promising methods to reduce the degradation of the cathode activity that is likely happening in this system. During the cathodic pulses, operating at -1.5 V or -1.7 V (v Ag/AgCl), the system operates as before, reducing CO_2 into CO over the silver cathode. During the anodic pulses, operating at -0.1 V, +0.1 V, +0.5 V, or +1.5 V (v Ag/AgCl), there is little to no formation expected of the desired products, and instead the potential goes towards changing the behaviour of the cathode to be able to produce CO in the subsequent cathodic pulse. All experiments were first conducted with an anodic pulse followed by a cathodic pulse, with this order kept for the entire duration of each experiment. The standard conditions used for the pulse electrolysis experiments are shown in Table 7.

Table 7 - Standard conditions for pulse electrolysis experiments.

Experimental condition	
Catholyte	0.5 M MEA in ChCl:EG 1:4 CO_2 loaded
Temperature	65 °C
CO_2 flow rate	15 ml/min
GC sampling time	2 min
Equipment	GC 7
Pulse Order	Anodic pulse followed by cathodic pulse. (repeated in this order for entire experiment)

6.2.1 One Initial Anodic Pulse (exp. 8)

The first experiment conducted using pulse electrolysis consisted of one initial anodic pulse of +1.5 V (vs. Ag/AgCl) for 40 seconds followed by a continuous reduction at -1.5 V (vs. Ag/AgCl) for approximately two hours. Figure 14 shows the FE of the initial pulse electrolysis investigation. The FE of CO production is relatively high at the start of the experiment immediately after the initial oxidation step pulse and slowly drops off to zero at around 80 minutes. For the first hour of operation, it has an average FE of CO production of 20.2 %, but importantly this is constantly decreasing. The current is also not stable and slowly decreases over the course of the experiment. This along with the drop in CO production indicates that there is still a change happening to at least one component of the system.



(a)

(b)

Figure 14- Faradaic efficiency (a) and current (b) for one anodic pulse of +1.5 V vs. Ag/AgCl for 40 seconds at the start followed by constant voltage of -1.5 V for two hours (exp. 8).

This clearly shows that an initial oxidation step at the start of the experiment leads to an increase in FE of CO production and slows down the rate of decrease with time as well. This system with an initial anodic pulse is able to produce CO for over an hour, compared to just 10 minutes with no anodic pulse. This proves that an oxidation step increases the overall efficiency of the system, however there is still a drop off in CO production that is not controlled by this one initial step, meaning that the production of CO is not stable. The subsequent section explores if an anodic pulse every 10 minutes of operation can make the system more stable and what the optimal conditions for this are.

6.2.2 Finding Optimal Pulse Conditions

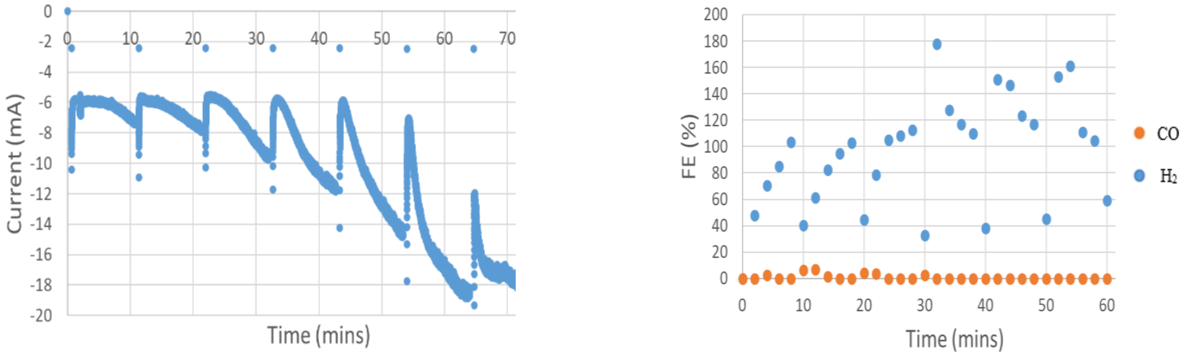
To determine the parameters of pulse electrolysis that are optimal for this system, a range of different anodic pulse time and potentials were used. The cathodic pulse potential and time were kept constant at -1.5 V (vs. Ag/AgCl) and 10 minutes initially in order to reduce the complexity and number of experiments that needed to be completed. Later experiments are conducted with both shorter reduction times and greater reduction potentials to see their effect on the system. It was decided to use an initial anodic pulse at the very start of the experiment in order to regenerate the cathode in case there was already changes occurring just during the heating process before the start of the experiment. The conditions used for all the pulse electrolysis experiments in this section are given in Table 7 below. It should be noted that for all the figures displaying the current of each experiment the anodic pulse is not included, this is to increase the clarity of the cathodic pulse current values.

Table 7 – General conditions for pulse electrolysis

Experimental conditions	
Catholyte	0.5 M MEA in ChCl:EG 1:4 **CO_2 loaded**
Temperature	65 °C
CO_2 flow rate	15 ml/min
GC sampling time	2 min
Equipment	GC 7

6.2.2.1 Anodic Potential of -0.1 V vs. Ag/AgCl

The faradaic efficiency of H_2 and CO production and the current of the cell are shown in Figure 15 for an anodic pulse potential of -0.1 V vs. Ag/AgCl for 40 seconds (exp. 9). It is clear that this combination of pulse conditions does not sufficiently regenerate the system, as can be seen from the very low FE of CO production and high FE for H_2 production. The average FE for CO production over the one hour of operation is only 0.9%, with most of this coming within the first half an hour. However, the figure shows from the profile of the FE of H_2 production that there is some changes occurring due to the anodic pulse for the first three pulses. Every 10 minutes, the FE of H_2 decreases and then starts to increase until the next pulse cycle starts. After the third pulse it is less clear how the pulses are affecting the H_2 production. Additionally, the current of the system is shown to quickly decrease from an average of -6 mA for the first pulse to -17 mA for the last pulse. This change in pulse across the operating time of only one hour suggests that this is not a stable system and is therefore harder to operate in the real world. It is clear that a negative anodic pulse potential is therefore not suitable for this system. The total FE being above 100% is an experimental error due to the previously mentioned issues with the inlet gas stream being contaminated.



(a) (b)

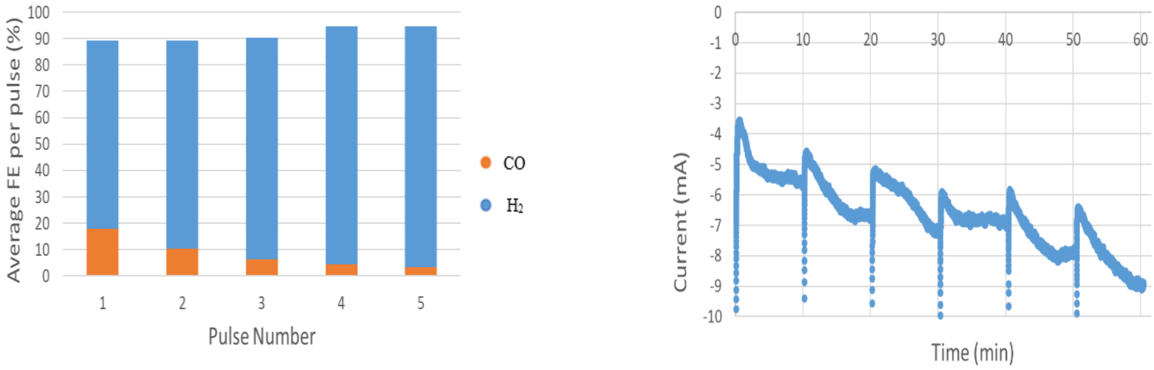
Figure 15 - The faradaic efficiency (a) and current (b) of the pulse electrolysis with -0.1 V vs. Ag/AgCl for 40 seconds (exp. 9).

6.2.2.2 Anodic Potential of +0.1V vs. Ag/AgCl

For an anodic potential of +0.1 V (vs. Ag/AgCl) a series of three different anodic pulse times were utilised, 5, 20, and 40 seconds, to give a wide range of possible conditions. The cathodic pulse conditions were kept constant at +1.5 V (vs. Ag/AgCl) for 10 minutes, this time was chosen as this was the longest time that the system could produce a sufficient amount of CO in the initial experiments not using pulse electrolysis.

Anodic Pulse of 5 Seconds, +0.1V vs. Ag/AgCl (exp. 10)

The results for using pulses of +0.1 V (vs. Ag/AgCl) for 5 seconds are shown in Figure 16. The average FE of CO and H_2 production are shown in Figure 10, and this shows that there is some CO being produced throughout the run time of approximately 1 hour. On average throughout the hour the FE is 5.6 % for CO. The current response also shows a somewhat stable profile, with the average current decreasing only 2.8 mA throughout the experiment. However, the FE of CO production is relatively low and is decreasing with each pulse from the second onwards, this suggests that the oxidation step is unable to fully regenerate the silver electrode in this configuration. This shows that pulse electrolysis produces better results than the standard operation of continuous reduction but that these conditions still need to be optimised.



(a) (b)

Figure 16 - Pulse of 5 seconds at +0.1 V vs. Ag/AgCl (a) average faradaic efficiency per pulse (b) current response.

While the average FE per pulse is useful to see how the FE of the system varies over a longer period of operation, it is less helpful at seeing what is happening in each individual pulse. Figure 17 shows the results of the experiment for +0.1V for 5 seconds, but this time with the FE every two minutes, not on average per pulse. This clearly shows how the FE of CO and H_2 is affected by the anodic pulse. It is clear that in the period immediately after the anodic pulse there is greater FE of CO production and lower FE of H_2 production. There is a clear suppression of the HER due to the anodic pulse. During the cathodic pulse there is an increase in H_2 production until the next anodic pulse and a decrease in CO production.

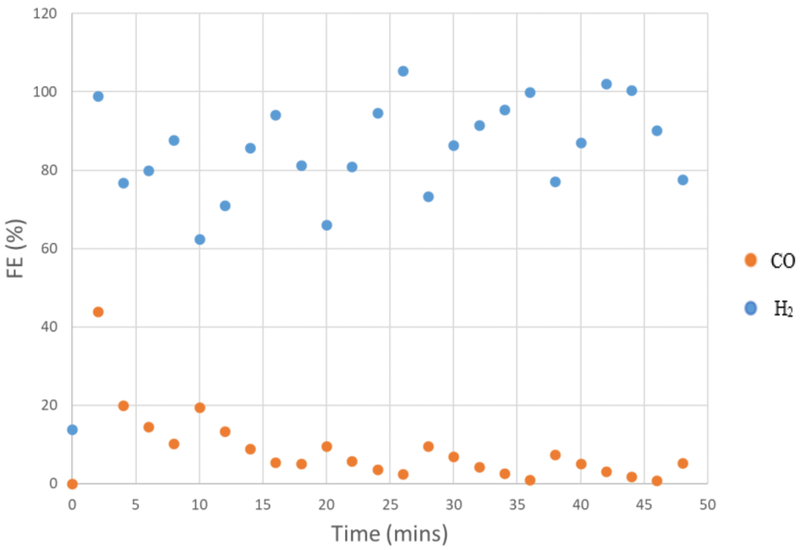
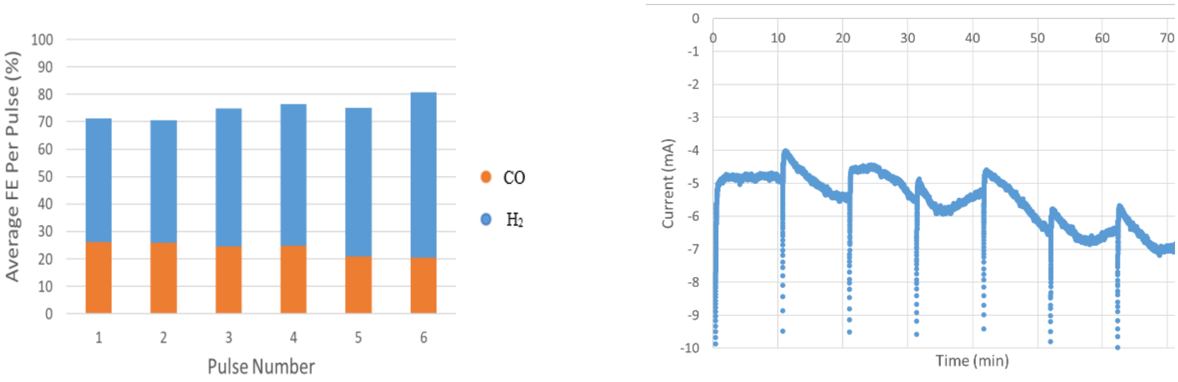


Figure 17 - FE, of using pulse of 5 seconds at +0.1 V vs. Ag/AgCl , every two minutes for CO and H_2.

Anodic Pulse of 20 Seconds, +0.1 V vs. Ag/AgCl (exp. 11)

The average FE for CO and H_2 per pulse and the current response, for anodic pulses of 20 seconds at +0.1 V (vs. Ag/AgCl) are shown in Figure 18. The average FE for CO production over the hour of operation for the cell is 23.7 %, which is substantially more than in the constant current set up which is 2.5 % for the same time frame. Additionally, it is clear that while there is a decrease in FE for CO production, this is only minor and there is still high FE for CO at the end of the experiment, never falling below 20%. This suggests that this set of pulse conditions, +0.1 V for 20 seconds, is regenerating the electrode and allowing the system to act in a stable way. This is also confirmed by the relatively stable current throughout the experiment as the average current during the first pulse is only 1.7 mA greater than that in the last pulse.



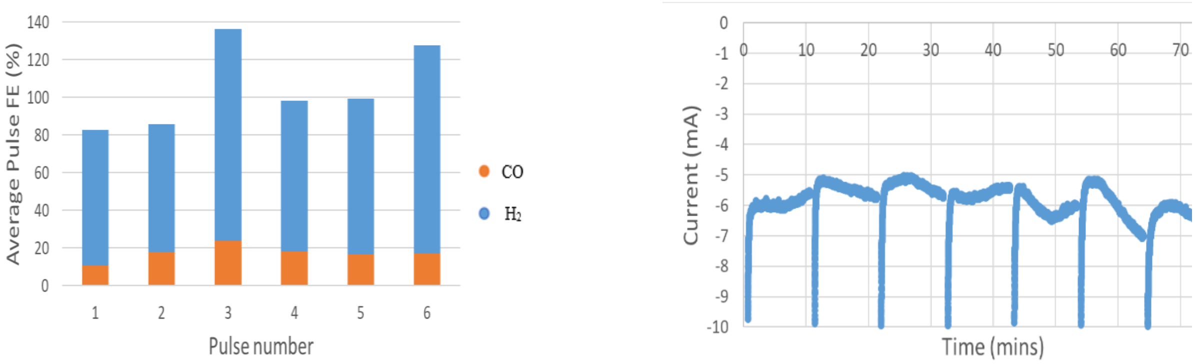
(a)

(b)

Figure 18 - Pulse of 20 seconds at +0.1 V vs. Ag/AgCl (a) average faradaic efficiency per pulse (b) current response (exp. 11).

Anodic Pulse of 40 Seconds, +0.1 V vs. Ag/AgCl (exp. 12)

The average FE for each pulse for CO and H_2 production and the current response for anodic pulses of 40 seconds at +0.1 V (vs. Ag/AgCl) are shown below in Figure 19. The average FE for CO production over the hour of operation for the cell is 14.2 %. In addition ,it is clear from the figure that there is only a very small decrease in the average current per pulse for the one hour of operation, only 0.1 mA difference. This indicates that this pulse condition of +0.1 V for 40 seconds is regenerating the electrode and allowing stable operation.



(a) (b)

Figure 19 - Pulse of 40 seconds at +0.1 V vs. Ag/AgCl (a) average faradaic efficiency per pulse (b) current response (exp. 12).

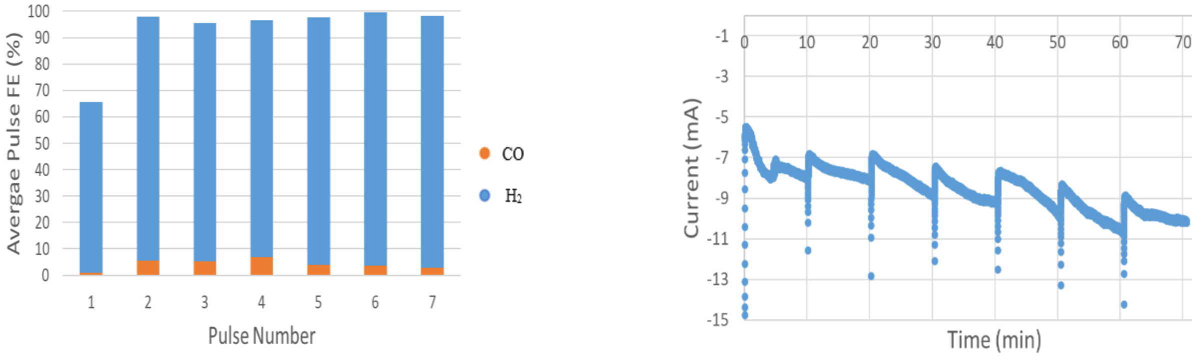
The results for the pulse electrolysis of anodic pulses of +0.1 V for various times have shown that pulse electrolysis, with positive anodic potentials, can provide a route to more stable operation of the system in question. The FE of CO production is much higher for operating the system for an hour than those without any pulses, up to nine times greater for the 20-second-long pulses. Importantly, there is CO formation throughout the entire hour of operation for all of these conditions in comparison to no pulse conditions in which it was only seen for 10 minutes. The reason for 20 seconds providing greater FE than 5 or 40 seconds is not able to be determined from these results but does warrant further investigation in future research through surface characterization of the electrodes and other methods. Further anodic potentials are explored below, to determine what the optimal conditions might be.

6.2.2.3 Anodic Potential of +0.5V vs. Ag/AgCl

This section presents the results of using an anodic potential of +0.5 V (vs. Ag/AgCl) for 5, 20, and 40 second pulses, with a reduction pulse of -1.5 V (vs. Ag/AgCl) for 10 minutes. The same cell setup is used as in previous sections with a CO_2 loaded catholyte, CO_2 purge into the cell, and an initial anodic pulse followed by a cathodic pulse of 10 minutes repeated for one hour.

Anodic Pulse of 5 Seconds, +0.5 V vs. Ag/AgCl (exp. 13)

The average FE per pulse for the production of the two gases of interest and the current response for anodic pulses of 5 seconds at +0.5 V are shown below. The average FE for CO production over the hour of operation for the cell is 4.3%. While this average FE of CO production is relatively low there is still CO formation for the entire hour, meaning that this is more stable than those experiments without pulse electrolysis. In addition to this it is clear from the figure that there is a decrease in the average current per pulse for the one hour of operation.

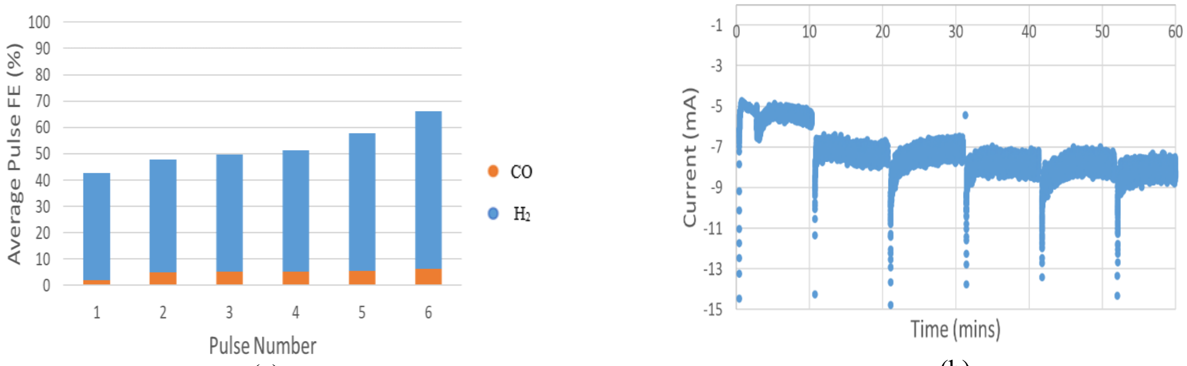


(a) (b)

Figure 20 - Pulse of 5 seconds at +0.5 V vs. Ag/AgCl (a) average faradaic efficiency per pulse (b) current response.

Anodic Pulse of 20 Seconds, +0.5 V vs. Ag/AgCl (exp. 14)

The average FE for each pulse and the current response of the cell, for anodic pulses of 20 seconds at +0.5 V (vs. Ag/AgCl) are shown below. The average FE for CO production over the hour of operation for the cell is 4.6 %. The FE is relatively low but does show a relatively stable level of production of CO over the experiment, even slowly increasing over the course of the hour. It is interesting to note that the H_2 and CO FE do not total to 100%, meaning that there is a relatively large amount of other unknown products forming. The average current for the one hour of operation is -6.9 mA, with a change from the first to the last pulse of roughly -3 mA.

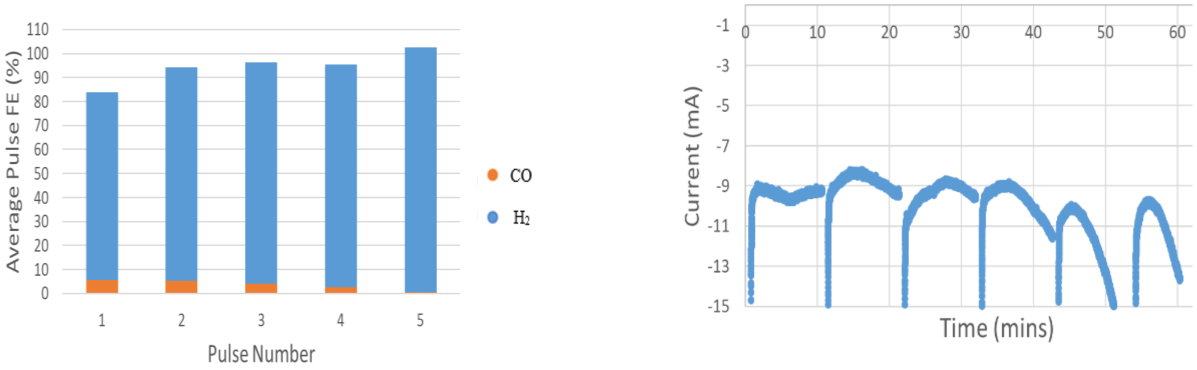


(a) (b)

Figure 21 - Pulse of 20 seconds at +0.5 V vs. Ag/AgCl (a) average faradaic efficiency per pulse (b) current response.

Anodic Pulse of 40 Seconds, +0.5 V vs. Ag/AgCl (exp. 15)

The results of the anodic pulse of 40 seconds at +0.5 V (vs. Ag/AgCl) are shown below. The FE of CO production is clearly unstable, decreasing with each pulse until it reaches close to 0 after the one hour of operation. The average FE for CO production over the experiment is just 3.7%. The current is also clearly unstable with large drop offs in current for the last two pulses, with drops of 5 mA during the fifth pulse alone. The reason for this large decrease in current in the last two pulses is unknown but does warrant further investigation in the future as it could indicate issues with the system.



(a) (b)

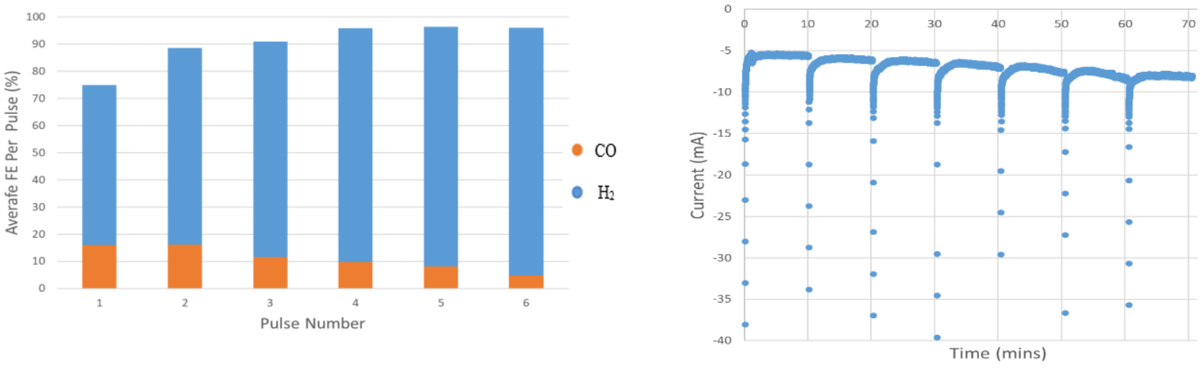
Figure 22 - Pulse of 40 seconds at +0.5 V vs. Ag/AgCl (a) average faradaic efficiency per pulse (b) current response.

6.2.2.4 Anodic Potential of +1.5 V vs. Ag/AgCl

The pulse experiments with an anodic potential of +1.5 V (vs. Ag/AgCl) and various anodic pulse times are presented in this section. The H-cell set up remains constant as in previous experiments with a CO_2 loaded catholyte, CO_2 purged into the cell, and an initial anodic pulse followed by a cathodic pulse repeated in this order for one hour. It is important to note that at potentials of +1.5 V it is possible that this is operating in the region where the electrolyte could be suffering from decomposition faster than in lower potentials, so extra attention needs to be paid to this aspect.

Anodic Pulse of 5 Seconds, +1.5 V vs. Ag/AgCl (exp. 16)

The results of the pulse electrolysis for +1.5 V for 5 seconds are shown below in Figure 23. The average FE for CO production for these conditions over the one hour of operation was 10.8%, with a change in current of 2.2 mA. With each cathodic pulse the average FE of CO production decreases for the operational time. The average current shows a small negative trend as the experiment progressed, with an overall average of -6.7 mA.

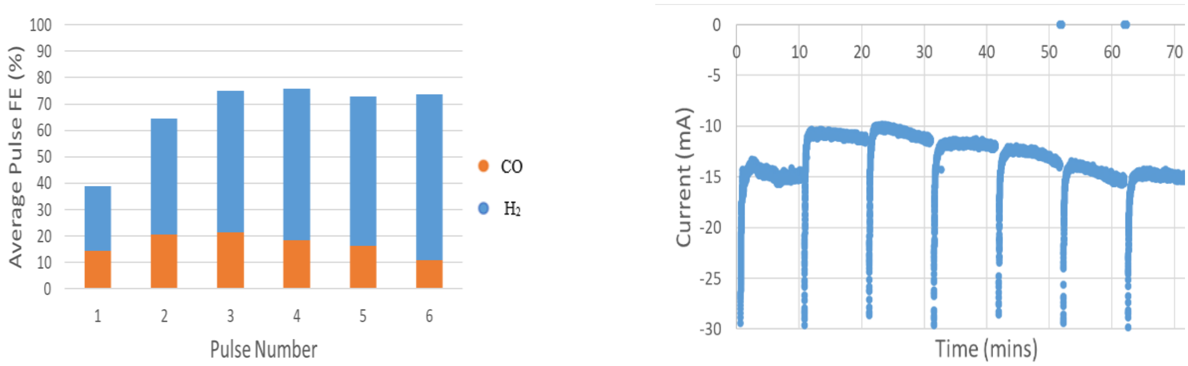


(a) (b)

Figure 23 - Pulse of 5 seconds at +1.5 V vs. Ag/AgCl (a) average faradaic efficiency per pulse (b) current response.

Anodic Pulse of 20 Seconds, +1.5 V vs. Ag/AgCl (exp. 17)

The anodic pulse of +1.5 V (vs. Ag/AgCl) for 20 seconds is presented in this subsection. It is clear from the FE shown in Figure 24 that the conditions are able to maintain a relatively stable operation for the one-hour time frame of this experiment. The average FE of CO production is 15.1 %, with the peak of the FE being at the third pulse when it reaches 21% and falling to 11% on the sixth pulse. The current also shows some stability with an average current across the operation of the cell of -11.3 mA, but there is still an overall decrease from the second to the final pulse.

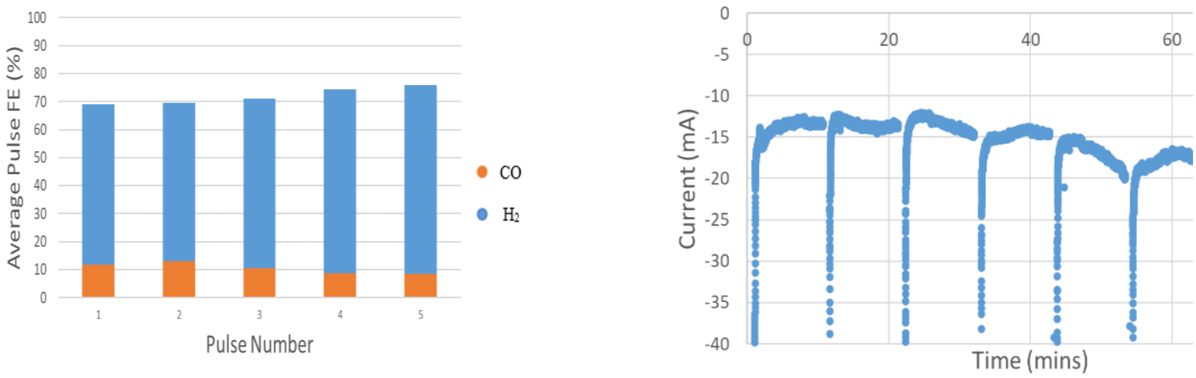


(a) (b)

Figure 24 - Pulse of 20 seconds at +1.5 V vs. Ag/AgCl (a) average faradaic efficiency per pulse (b) current response.

Anodic Pulse of 40 Seconds, +1.5 V vs. Ag/AgCl (exp. 18)

The results of the anodic pulse of +1.5 V (vs. Ag/AgCl) for 40 seconds are presented below. It is clear from the FE for CO that the conditions can maintain a relatively stable operation for the first half an hour but that the FE starts to decrease after this. The average FE of CO production is 9.7 %, with a downwards trend seen after the second pulse. The current also shows a similar trend to CO FE, with a decrease in average current per pulse being seen after 20-30 minutes of operation. The average current for the hour of operation is -12.77 mA, with an overall decrease in current per pulse as the cell continues to operate.

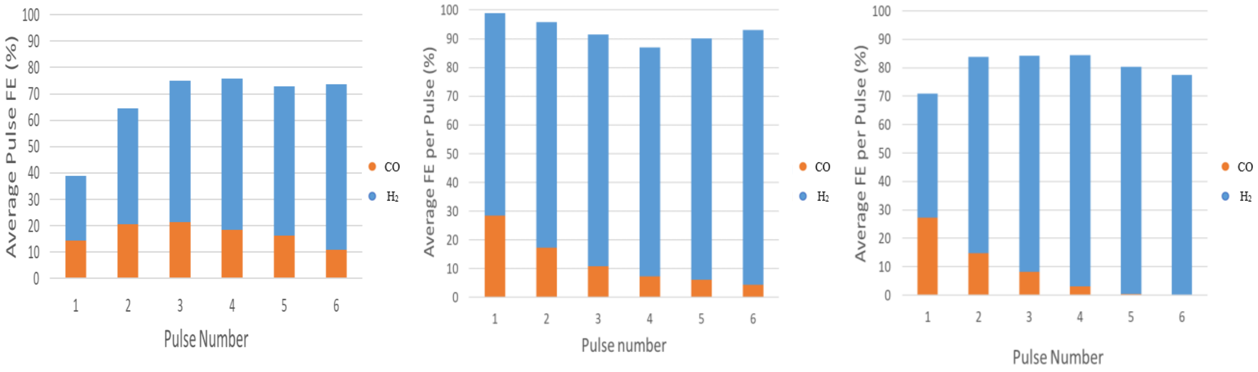


(a) (b)

Figure 25 - Pulse of 40 seconds at +1.5 V vs. Ag/AgCl (a) average faradaic efficiency per pulse (b) current response.

6.2.2.5 Repeat Experiments: +1.5 V vs. Ag/AgCl for 20 Seconds

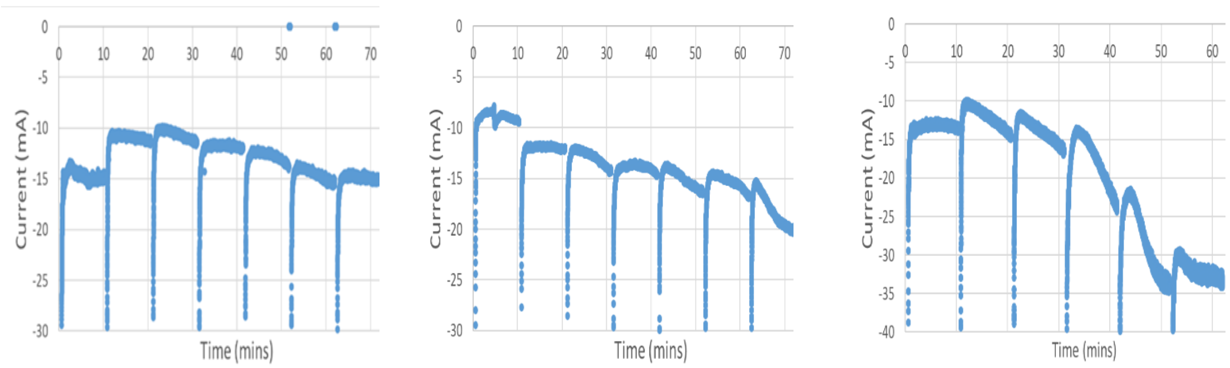
The results of this initial investigation into the pulse electrolysis's effect on the system have been difficult to replicate reliably in the time frame of this project. The FE of the repeated experiment with a 1.5 V anodic potential for 20 seconds are shown below. The average FE of CO production for repeat 1, 2, and 3 are 15.1%, 12.7%, and 8.9%, respectively. Repeat 1 and 2 have a similar average FE over the course of the one-hour experiment but it is clear from the figures that the trend seen in this over the two experiments are very different. Repeat 2 suffers a much greater decrease in FE compared to repeat 1, meaning that these two experiments do not yet prove that the experiment is repeatable. Additionally, repeat 3 has two final pulses in which almost no CO is detected, making this repeat different than the others.



(a) (b) (c)

Figure 26 – Average FE per pulse for CO and H_2 *for the repeated experiments of +1.5 V vs. Ag/AgCl for 20 seconds anodic pulses and 10 minutes of reduction at -1.5 V vs. Ag/AgCl (a) repeat 1 (b) repeat 2 (c) repeat 3, experiment 17, 19, and 20, respectively .*

The currents of these three repeated experiments also show the challenges of getting accurate repeatable results. The average current for the one hour of operation for the three experiments are -11.3 mA, -12.9 mA, and -19.6 mA for repeat 1, 2, and 3, respectively. While the repeats 1 and 2 have roughly similar profiles of decreasing currents over the course of the hour, they do have different average currents. Additionally, the profile of repeat 3 is completely different than the previous two, with much larger and steeper drops in current over the course of the experiment and within the pulses themselves.



(a) (b) (c)

Figure 27 – Current for the repeated experiments of +1.5 V vs. Ag/AgCl for 20 seconds anodic pulses followed by 10 minutes of reduction at -1.5 V vs. Ag/AgCl (a) repeat 1 (b) repeat 2 (c) repeat 3.

The main differences between each experimental run are the silver electrode, the electrolyte, and the temperature of the cell. As the temperature of the cell is closely monitored and the electrolyte solution is carefully pipetted into the cell each time, it is unlikely that these are causing the instability seen between experimental runs. Instead, it is possible that there is some degradation of the silver working electrode that is acting as the cathode. As detailed in Section 5, the electrodes are used for one experiment, analysed for their surface characteristics, and then cleaned for further use. This cleaning is done through polishing the electrode until a mirror-like surface is formed, and then using a sonic bath to remove any further particles on the surface. It has not been possible to determine if this is the reason for the inability to produce repeatable experiments, and the project scope has not allowed time to investigate the exact mechanism by which this could be happening.

There are also issues that are already known with the thermocouple that is used in the system, this is placed in the anode compartment. It has previously been seen that its presence in the system leads to some metal deposition on the electrodes in both compartments, which can have an effect on the activity of these electrodes. To avoid these issues the thermocouple is wrapped in Teflon tape to avoid the metal coming into contact with the solution. To determine if this was effective at stopping metal impurities entering the system ICP analysis was completed on the anolyte and catholyte. The results of this are presented in Appendix D for a selected number of samples. Looking specifically at nickel impurities shows us that repeat 3 has nickel concentrations of 113.3 ppm in the anolyte, compared to 3.8 and 1.7 ppm in the anolyte in repeat 1 and 2 respectively. This large difference in nickel concentration has the possibility of interfering with the results and can partially explain why repeat 3 is very different than repeats

1 and 2. It is more difficult to determine from the ICP data what could cause the issues between repeats 1 and 2.

The lack of repeatability of the results is an issue for the final conclusions of this report; however, as the timeframe of the project was limited it was decided that obtaining data for further experimental conditions was more advantageous. Further work by other members of the research team that will be completed after this project will attempt to investigate further these issues, with a focus on the surface characterisation of the electrodes after each experiment to determine if any changes are taking place. Greater care must also be taken in future experiments to ensure that the thermocouple is sufficiently isolated from the anolyte.

6.2.2.6 Summary of Results for 10 Minutes of Reduction and Various Anodic Conditions

The results of the experiments above using a 10-minute reduction time with -1.5 V (v Ag/AgCl) of cathodic potential with various anodic potentials are presented in Table 8. The results clearly show that the optimal FE of CO production occurs at conditions of relatively low anodic potentials of +0.1 V (v Ag/AgCl) for an anodic pulse time of 20 seconds. These conditions also allow for a relatively stable FE of CO over the course of one hour, with the first pulse having an FE of 26% and the final pulse having an FE of 20.5%. Another interesting result from these experiments is that the middle anodic potential studied of +0.5 V (v Ag/AgCl) has the lowest FE of CO production for all positive anodic pulse times. Finally, all positive anodic potentials were able to maintain CO production for much longer periods of operation than those experiments without any pulse electrolysis being used. This clearly shows that using short positive potential anodic pulses alongside a reduction potential of -1.5 V (v Ag/AgCl) is a viable method for increasing the CO production in this system.

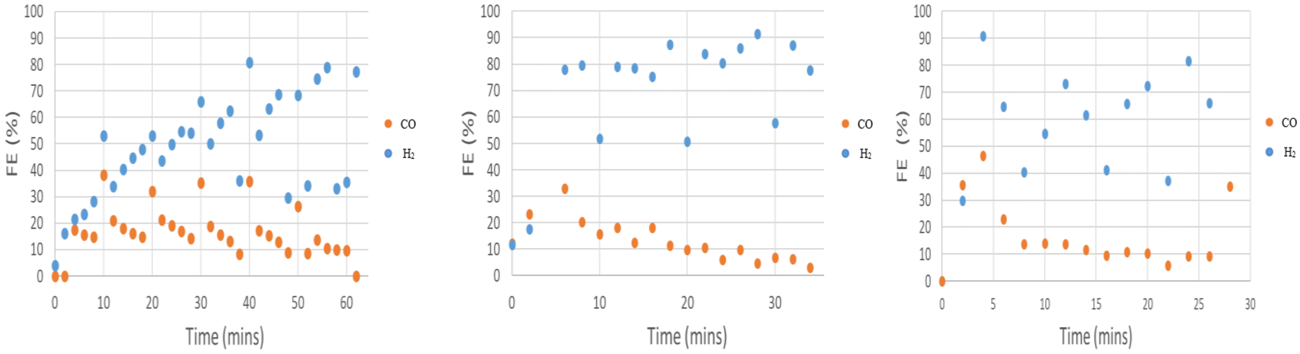
Table 8 – Summary of FE for CO production for using -1.5 V (vs. Ag/AgCl) reduction potential vs. Ag/AgCl for 10 minutes with various anodic pulse conditions.

	Anodic time (seconds)		
Anodic potential (V)	5	20	40
- 0.1			0.9 %
+ 0.1	8.4 %	23.7 %	14.2 %
+ 0.5	4.3 %	4.6 %	3.7 %
+ 1.5	10.8 %	15.1 %	9.7 %

6.2.3 Shorter Cathodic Pulse Time: 10, 5, 2.5 Minutes

The ten-minute cathodic pulse used for the initial experiments was chosen due to the fact this was the maximum time that the initial system without pulse electrolysis seemed to keep a relatively high FE of CO production. However, ten minutes is a relatively long time for this type of system, so this section investigates the use of shorter pulses to increase the FE of CO production. The conditions used for the anodic pulse were chosen as +1.5 V (vs. Ag/AgCl) for 20 seconds, as this condition had good overall FE in the initial investigation. The cathodic pulse time was lowered to 5 and 2.5 minutes always with a -1.5 V (vs. Ag/AgCl) reduction potential.

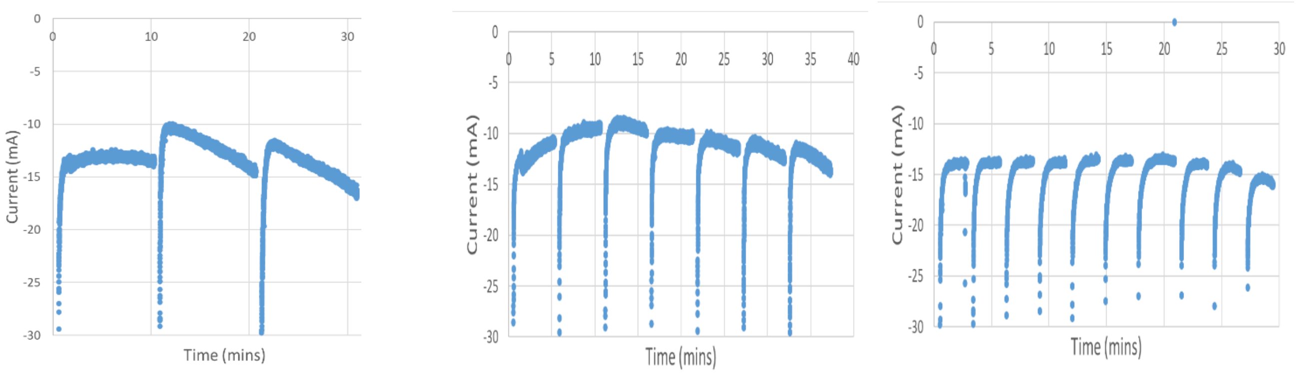
The comparison between the three pulse times, including their FE and current response are shown below. The most important result of this experiment is that there is not a large dependency between reduction time and FE of CO production. For the first half an hour that the experiments ran the average FE of CO production was 17.3%, 17.5%, and 14.5% for a 10, 5, and 2.5-minute reduction period, respectively. Particularly for 10 and 5-minutes reduction times the difference is not considered to be significant with the errors that are likely present in the experimental setup. It is recommended that both of these experiments run for longer periods of time, at least one hour, in order to see their longer-term performance in the future. The 2.5-minute reduction time experiment has more consistent FE of CO production after the first 10 minutes than the other reduction times, however as the overall FE is lower it is of limited interest. It should be noted that a small error was made in the setup of the 2.5-minute reduction time experiment, where one of the reduction pulses at approximately 20 minutes into the experiment lasted for 5 minutes. This will have changed how the system behaved but it is not considered to have had a large enough impact to completely discount this result.



(a) (b) (c)

Figure 28 - FE every 2 minutes for CO and H_2 for anodic potentials of +1.5 V vs. Ag/AgCl for 20 seconds followed by reductions potentials of -1.5 V vs. Ag/AgCl for (a) 10 minutes (b) 5 minutes (c) 2.5 minutes.

Figure 29 shows the current performance for each of these experiments with various reduction times. Clearly, all are able to maintain a somewhat stable current during operation of the cell but there are still changes present. All three reduction times were able to maintain currents between 10 mA and 16 mA for the first half an hour of operation. In particular, the reduction time of 2.5 minutes is able to maintain a very stable operation for 20 minutes, however this starts to drop off after 20-25 minutes. With the limited running time of the two experiments with short reduction times, it is difficult to determine how their current responses compare, and it is recommended to do these both again for longer periods of time.



(a) (b) (c)

Figure 29 – Current of the cell for anodic potentials of +1.5 V vs. Ag/AgCl for 20 seconds followed by reductions potentials of -1.5 V vs. Ag/AgCl for (a) 10 minutes (b) 5 minutes (c) 2.5 minutes.

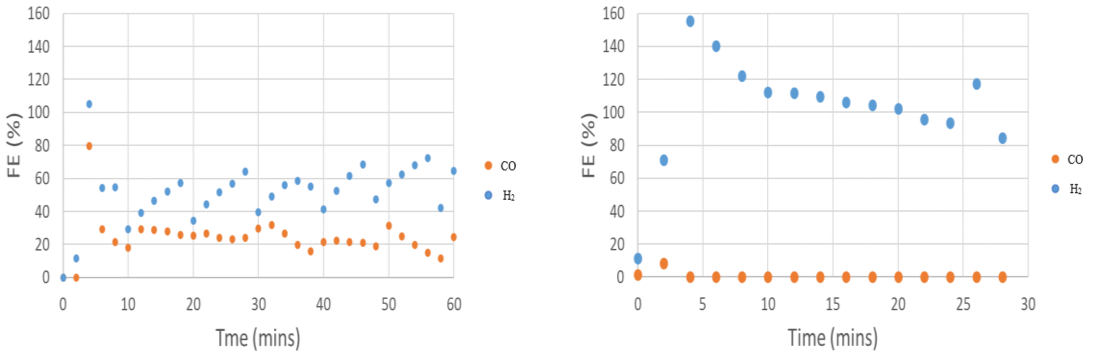
The silver cathode of each of these experiments is pictured in Figure 20. This shows a similar end result for each of the experiments with a grey textured layer forming on the section of the cathode exposed to the catholyte. It is important to note that the part of the cathode that is exposed to the catholyte, and therefore is active in the reduction process, is the small circular section in the middle in which this deposit of material is seen. This suggests that similar reactions are occurring in each of the conditions. This result agrees with the FE and current responses of the systems being reasonably like each other.

(a) (b) (c)

Figure 30 – Cathode for anodic potentials of +1.5 V vs. Ag/AgCl for 20 seconds followed by reductions potentials of -1.5 V vs. Ag/AgCl for (a) 10 minutes (b) 5 minutes (c) 2.5 minutes.

6.2.4 Greater Reduction Potential Using Pulsed Electrolysis

As explored in the initial investigation of the system, different reduction potentials are also possible for the standard system without pulse electrolysis, namely -1.7 V (vs. Ag/AgCl). It is interesting therefore to determine if the same effect of using pulse electrolysis is also possible at this reduction potential and if it might even be more efficient than a reduction potential of -1.5 V. Figure 31 below shows the results of using -1.7 V as a reduction potential for 10 minutes, with anodic pulses of +0.1 V for 20 seconds. As can be seen clearly from the FE of CO production, it is not suitable for use as there is little CO production and none after the first 10 minutes of operation. This is in comparison to the use of -1.5 V for the same anodic pulse conditions, which was able to have relatively stable production of CO for the entire hour of the experiment. There is also no strong dependence of the FE_{H2} on the anodic pulses unlike in the -1.5 V experiment, but the reason for this cannot be determined directly from these results. The results of the -1.7 V experiment were successfully replicated three times, and the data for these is available in the appendix.



(a) (b)

Figure 31 – FE of CO and H_2 production every two minutes applying anodic pulses of +0.1 V vs. Ag/AgCl for 20 seconds and reduction pulses of 10 minutes and (a) -1.5 V vs. Ag/AgCl and (b) -1.7V vs. Ag/AgCl .

The silver cathode and how it behaves during the operation of the cell is one of the most interesting factors in this experimental setup. There was insufficient time in this project to perform detailed examination of the cathodes using methods such as scanning electron microscopes or other analytical methods. However, the cathodes were photographed after each experiment instead. Below are the cathodes for the pulse electrolysis experiments using anodic pulses of +0.1 V (vs. Ag/AgCl) for 20 seconds with either -1.5 V or -1.7 V (vs. Ag/AgCl) for the cathodic potential. The appearance of the section of the cathodes that are in contact with the solution are very different, suggesting that different reactions are occurring in each case.

The cathode using a reduction potential of -1.5 V has a dark grey colour with a raised textured solid formed on it. This contrasts sharply with the cathode for -1.7 V, which has a black coating on it with no raised texture. It is possible that this dark coating on the -1.7 V cathode is inhibiting the production of CO in some way, but further analysis is needed. It is also likely that the species being deposited on the cathode for -1.5 V are helping to increase the CO production in some way. The ICP results also do not provide a clear explanation of what the formations on the surface of the electrodes might be, only that there is more nickel present in the -1.7 V catholyte and there is also more SO_4 ions present as well. This increase in SO_4 suggests that there is more transfer between the cathode and anode compartments at higher reduction potentials, this is also shown by the lower concentration of Cl in the sample from this higher potential experiment. This could also explain the difference seen in H_2 and CO formation.


(a) (b)

Figure 32 – Comparison of electrodes for (a) -1.5 V vs. Ag/AgCl and (b) -1.7 V vs. Ag/AgCl of reduction potential with a +0.1 V vs. Ag/AgCl 20 second anodic pulse.

6.2.5 Silver Cathode Analysis

The final appearance of the silver cathodes is an indication of how the cell and the electrolyte are performing. It is shown in previous sections that those experiments in which a CO_2 loaded catholyte is used a dark grey textured deposit is formed on the surface of the cathode. This directly contrasts with the cathode for when an argon loaded catholyte is instead used in which no such deposit is seen. This means that the species being deposited are directly due to the reactions occurring in the system with the CO_2 present. In addition, when a temperature of 40°C is used with a CO_2 loaded catholyte there is also no deposits on the cathode surface. However, the most interesting comparison for which there is photographs available for the comparison is between using and not using pulsed electrolysis. Figure 33 shows the cathodes for the experiments utilising -1.7 V (vs. Ag/AgCl) as the reduction potential, one with and one without anodic pulses. It is clear from these cathodes that the deposition of material is linked to the pulse electrolysis effects.

(a) (b)

Figure 33 – Comparison of electrodes for (a) -1.7 V vs. Ag/AgCl (exp. 3) and (b) -1.7 V vs. Ag/AgCl (exp. 23) of reduction potential with a +0.1 V vs. Ag/AgCl 20 second anodic pulse.

For each of the silver cathodes it would have been interesting to see how this material is deposited with time. This could have been completed by using different experimental times and comparing the cathodes of each of these. It would have been interesting to see how this build-up of material on the cathode aligned with changes in the current and FE seen in the different experiments. Additionally, to gather more meaningful data from these cathodes more thorough analytical techniques need to be used other than visual analysis. Determining which material is being deposited on the cathode and its quantity are both interesting parameters that would help build an understanding of the system if understood in more detail.

7 Discussion

The results presented in Section 6 show that the proposed system of using the DES of 1:4 choline chloride to ethylene glycol coupled with MEA for the system of electrochemical CO_2 reduction is possible. However, the results clearly indicated that the system still has some issues, including instability and relatively low FE of CO_2 reduction.

7.1 Discussion of Initial Experimental Results

The initial experimental results, investigating the system's ability to reduce carbon dioxide and its stability, are promising. They show that the system can successfully reduce carbon dioxide into the desired product of carbon monoxide. It has been shown that this production of CO is conclusively down to the reduction of CO_2 and not through other means such as electrolyte decomposition. However, the system is only able to produce CO for approximately ten minutes while operating at -1.5 V vs. Ag/AgCl and -1.7 V vs. Ag/AgCl at 65 °C, and not at all when operating at 40 °C. This limited operation time is not suitable for industrial applications that would be required to run for many hours continuously before parts could be replaced.

However, this work is particularly interesting when compared to work utilising aqueous MEA as the electrolyte medium. As found in the literature review, the FE of CO production in systems similar to the one in this project are between 2.3% and 12.4 %, however this is conducted at lower voltages vs. Ag/AgCl [14]. This means that this system potentially has greater ability to be used in electrochemical CO_2 reduction than the standard aqueous MEA solution. Interestingly however, the dependence of FE_{CO} on reduction potential is not the same as with the aqueous MEA solution where it decreases with more negative voltages, which indicates that the two systems do not behave in the same way [14].

In addition to the limited operational time that the system can be run for during the steady state reduction operation, the FE is still lower than desired. At its peak at approximately 3 minutes into the operation of the cell, the FE of CO production is around 38% and 62% for H_2. While this ratio of FE of CO to H_2 is better than what is achieved with aqueous MEA solutions in literature, there is still a relatively large amount of H_2 being produced. The improvement in this CO to H_2 ratio is most likely due to the non-aqueous nature of the catholyte in this project, and also possibly due to the more efficient use of protons that are transferred through the Nafion-117 membrane into the cathode compartment.

There are also drawbacks with the design of this section of the project, mainly with the limited number of conditions used as only two temperatures and three potentials are used. This makes it difficult to determine the optimal conditions for the system. It would have been interesting to also explore how the system works with different loadings of the catholyte solution as well as possibly how it works as a flow cell with a flow of catholyte through it. Furthermore, there are issues with being unable to fully account for the full range of products being formed, as exhibited through the total FE of products formed being less than 100%. This is particularly visible when using the higher potential of -1.7 V vs. Ag/AgCl reference electrode. Additionally, these initial experiments are not repeated multiple times due to the time constraints of the project and the time required to run each experiment. This alongside the issues seen with the repeatability of the pulse electrolysis results means that the results may not be fully accurate. However, these initial findings and observation helps us for further steps and exploration.

7.2 Discussion of Pulsed Electrolysis

The results of the pulsed electrolysis section are promising for the viability of the system. The FE seen for CO production, and therefore CO_2 reductio, are an average of 23.7 % for an hour of operation for an anodic pulse of +0.1 V vs. Ag/AgCl for 20 seconds with a reduction pulse of -1.5 V vs. Ag/AgCl for 10 minutes. This is much higher than most of the experiments in this project, but the most encouraging part of this result is the relative stability of the system over the course of the operation. The FE of CO per pulse drops only 6% over an hour of operation, from 26 % to 20 %. Additionally, the average current per pulse only decreases by 2.1 mA over the hour of operation as well. This is not only better than the results of the experiments without pulse electrolysis being used, but it is also better than those seen for a constant reduction potential only using MEA solutions.

However, several parameters are difficult to fully understand from these results and the exact mechanisms that are causing issues for the cell are not entirely clear. The reason for the positive anodic potentials that +0.5 V vs. Ag/AgCl should be the least good at regenerating the system and helping to keep CO production levels high is not clear. Additionally, it is unclear from these results why the best CO production is seen at +0.1 V vs. Ag/AgCl for 20 seconds and not for 5 or 40 seconds, this is also the case for the anodic pulse times. The pulse electrolysis has been proven to help keep CO production going for up to an hour but has not been used for any longer than this. Clearly, determining the maximum run time for the components in the cell would be of interest, and also analysis of the components after longer runs would help to build a deeper knowledge of the system.

The difference seen between the pulsed experiments utilising -1.5 V and -1.7 V (vs. Ag/AgCl) for the reduction potentials are also an interesting result from this project that is not fully explained by the data gathered. From the photographs of the silver cathodes, it is clear that the reaction happening in the cathode compartment is not identical in each of the experiments, as the material deposited is very different in colour and texture. In addition to this from the ICP results there is clearly more transfer of material form the catholyte to anolyte at greater reduction potentials, with over twice the concentration of SO_4 in the catholyte in the experiments with greater reduction potentials. The reason for this difference is not clear but this warrants further study to investigate how it is affecting the production of gases in the cell.

This section of results, while interesting, does have issues with the experimental design and how this affects the results. Firstly, it would be interesting to examine a greater range of operational conditions for the pulse electrolysis. Literature suggests that shorter anodic times are possible and if the CO production was sufficiently high this would be optimal due to the increased time that the desired products are produced. The lack of any detailed analysis of the cathodes after the experiments is a large gap in the experimental plan that hinders the understanding of these results. Finally, for many of the experiments, the total FE of the known products is well below 100%, meaning that either product is escaping the system or there are other products formed that are undetected. This means that the full efficiency of the system is hard to analyse due to a lack of understanding of the system.

8 Conclusions

The system of using a DES and amine mixture of choline chloride, ethylene glycol and MEA has been successfully identified and proven to be a viable electrolyte for use in electrochemical CO_2 reduction. It has proven to be successful in allowing the formation of CO over silver cathodes at constant reduction potentials of -1.5 V and -1.7 V vs. Ag/AgCl at 65 °C. The system is able to produce relatively good levels of CO, with FEs of between 20 % and 40 %. However, this is only found to be able to operate for less than ten minutes before CO production drops off and H_2 production dominates. This means that the system is not suitable for use in constant potential operation. This can be at least partially solved through the use of pulsed electrolysis. The pulsed electrolysis, specifically using positive anodic potentials, has been proven to allow a steadier rate of CO production and therefore CO_2 conversion when compared to constant voltage operation. This was able to increase the FE of CO production in the system by over nine times over the course of one hour of operation when using anodic potentials of +0.1 V vs. Ag/AgCl. Importantly, both the constant potential operation and the pulse electrolysis operation were able to exhibit better FE than literature experiments which used aqueous MEA solutions, proving the viability of this new electrolyte [14].

The system of using the DES of choline chloride : ethylene glycol in a mole ratio of 1:4 coupled with the amine MEA as the electrolyte for electrochemical CO_2 reduction is very promising. If this technology can be successfully implemented, it can provide a viable route to form energy carriers and other chemicals from CO_2 using renewable energy generated from sources such as solar and wind. However, there still some issues remain with the system, in particular the long-term operation, which was not explored in detail in this project, and how the silver cathode acts during operation of the system is currently poorly understood. However, this project provides a good foundation on which future research can be complete, particularly focusing on longer term operation, reducing electrode degradation, and using a wider range of operating conditions. The recommendations from this project for future work are detailed in Section 9.

9 Further Work

The work presented in this project is a solid foundation on which additional work can be completed in order to further the development of this key technology. This includes using a much larger range of conditions such as temperature, MEA mole ratios, and pulse times, using flow cells to more accurately replicate industrial processes, and working to understand the degradation of the working electrode throughout the operation of the cell.

For completeness of the scientific work and to prove the system is suitable for use, it is important that the results are further repeated for the conditions used. This could focus on the use of new electrodes and new membrane for each experiment, or an investigation into how to more thoroughly regenerate the working electrode between experiments. Additionally, focus should be placed on ensuring that there are no impurities introduced into the system through the thermocouple or other components of the cell as well. A larger focus should be placed on surface characterisation to understand how the electrode is affected by operating in the cell which will give indications if the electrode is being degraded or poisoned during operation. These characterisation techniques such as SEM-EDS will also provide a better indication of the surface morphology changes and also to see how metal impurities in the solutions impact the surface of the electrodes. Understanding this is not only important for replicating the experimental results but also for how the system will operate in industrial settings.

The use of a flow cell in order to more accurately reflect the conditions that would be used in industrial scale equipment would be beneficial. A constant flow of new electrolyte into the cell will most likely affect the way that the system behaves during operation. Of particular interest is how the FE of the CO production is affected by this change to a flow system. The constant flow of new catholyte over the cathode might change how the electrode activity decreases over time. Additionally, as pulse electrolysis has proven to be successful for the batch H-cell, using similar conditions in a flow cell setup would allow a direct comparison between the two processes.

Furthermore, it is recommended that the system is explored for a wider range of conditions including total operating time, temperature, CO_2 purge rate, and pulse times. There are clear benefits in reduced heating costs to investigate the effects of temperatures between 40 °C and 65 °C. The CO_2 purge rate was set at 15 ml/min to try to keep the catholyte saturated with CO_2 at all times, however it is possible that this is not the case. Conducting experiments with additional flow rate of CO_2 would allow this to be determined. The maximum time that the system can produce CO is also of interest to investigate, as for industrial applications the cell would be expected to perform this role for many hours.

Lastly, the literature suggests that even shorter pulse times are possible for use in similar systems [6]. In particular, shorter anodic pulse times would be interesting to investigate as there is no product formation during these times so reducing them to the minimum possible would be a better use of the system. For similar systems, these anodic pulse times can be even less than one second in length [6]. However, the results of this project do suggest that 20 seconds is better than 5 seconds, it is unclear if making the anodic pulses any shorter would be beneficial for the system. Reducing the cathodic pulse times is also interesting but is less important if the product formation remains relatively high and stable during these times.

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Appendix A – Solvent Preparation

The solvent and electrolyte were prepared as described in the experimental section of this report, the exact amount of each component added is shown. It should be noted that the final step of the solvent preparation is to load it with CO_2 until it is saturated, it is however not possible due to the design of the experiment to confirm how much CO_2 has been absorbed.

Table 8 - Solvent preparation, mass of components added.

Chemical name	Amount added
Choline Chloride	200.10 g
Ethylene Glycol	350.71 g
MEA	15.91 g

Appendix B –Example Calculations for Electrochemical Experiments

This appendix has the raw data for the chronoamperometry electrochemical experiments for each of the experiments. This includes the current response of the system, and the gas peak areas for H_2 and carbon monoxide from the gas chromatography machine.

Due to the incredibly large amount of data produced by these experiments it is not practical to list it all in its entirety in this document. For this reason, the first 20 minutes of the experiment utilising an anodic pulse of +1.5 V (v Ag/AgCl) for 20 seconds and a cathodic pulse of -1.5 V (v Ag/AgCl) for 10 minutes is listed. This gives an indication of how the calculations were carried out for all experiments for their entire duration. The first results analysed are the current response, this is presented in Table 9. The average of the current per pulse is also calculated, this is done from 30 seconds into cathodic pulse until the end of the cathodic pulse. This average found is then used as the average current for the preceding anodic and the cathodic pulse. This process is not shown in this section due to the high number of data points required.

Using the GC calibration data that is obtained during the calibration setup of the equipment every few weeks it is possible to convert the peak areas obtained by the GC into concentrations in the units of Parts Per Million (PPM). This is done by using a gas with a known concentration of the gases of interest in it for the calibration and then comparing the peak areas in the experiment with the ones from the calibration. The partial current is then found using Equation 7. This calculation makes the assumption that all of the gas of interest present in the GC is produced in the cell, this is a valid assumption as for most experiments the gas line feeding the cell is not contaminated and is stable.

$$Partial\ Current = \frac{P \times flowrate \times F}{R \times T} \tag{7}$$

From this partial current for each of the gases of interest it is relatively simple to calculate the faradaic efficiency of producing each gas. This is done by dividing the partial current by the total current measured in the cell at the time of detection. This is done using the average current per pulse, as it was decided that it is impractical to use the exact current due to the slow nature of the GC sampling. The results of this are shown in Table 9.

Table 9 - Example calculations for electrochemical experiments

Time	Avg. current (mA)	Relative Peak Area H_2	Relative Peak Area CO	H_2 Concentration (ppm)	CO Concentration (ppm)	H_2 Partial Current (mA)	CO Partial Current (mA)	H_2 FE (%)	CO FE (%)
0	-14	0,0027	n.a.	94,2275	0,0000	0,20	0,00	1,5%	0,0%
2	-14	0,0276	n.a.	963,2144	0,0000	2,07	0,00	14,8%	0,0%
4	-14	0,2616	0,0187	9129,5972	1918,7216	19,66	4,13	140,6%	29,5%
6	-14	0,125	0,0105	4362,3840	1077,3570	9,40	2,32	67,2%	16,6%
8	-14	0,1163	0,0083	4058,7621	851,6251	8,74	1,83	62,5%	13,1%
10	-14	0,0403	0,0053	1406,4326	543,8088	3,03	1,17	22,1%	8,5%
12	-14	0,103	0,0101	3594,6044	1036,3149	7,74	2,23	57,1%	16,5%
14	-14	0,1159	0,0095	4044,8024	974,7516	8,71	2,10	64,2%	15,5%
16	-14	0,1227	0,0084	4282,1161	861,8856	9,22	1,86	68,0%	13,7%
18	-14	0,1277	0,007	4456,6115	718,2380	9,60	1,55	70,8%	11,4%
20	-14	0,0327	0,0033	1141,1997	338,5979	2,46	0,73	18,2%	5,4%

Appendix C – Experiment Naming Convention

The experiments conducted in this project are given codes in order to differentiate them from each other. These codes are not used throughout this report but are used in the appendices for the HPLC and ICP results. All experiments are conducted in the same H-cell, with a silver polished cathode, a platinum anode, an anolyte of 0.5 M sulphuric acid, and a nafion-117 membrane separating the compartments. All potentials are measured against Ag/AgCl.

Table 10 - List of experiments

Code	Experimental Conditions
Exp. 1	Constant reduction potential of -1.3 V at 65°C with a CO_2 loaded solution
Exp. 2	Constant reduction potential of -1.5 V at 65°C with a CO_2 loaded solution
Exp. 3	Constant reduction potential of -1.7 V at 65°C with a CO_2 loaded solution
Exp. 4	Constant reduction potential of -1.5 V at 65°C with **not** CO_2 loaded solution
Exp. 5	Constant reduction potential of -1.7 V at 65°C with **not** CO_2 loaded solution (repeat 1)
Exp. 6	Constant reduction potential of -1.5 V at 40°C with a CO_2 loaded solution
Exp. 7	Constant reduction potential of -1.7 V at 40°C with a CO_2 loaded solution
Exp. 8	One initial anodic pulse of +1.5 V for 20 seconds followed by continuous reduction at -1.5 V, 65°C, CO_2 loaded solution
Exp. 9	Pulsed electrolysis, 65°C, CO_2 loaded solution. -0.1 V 40 seconds, -1.5 V 10 minutes
Exp. 10	Pulsed electrolysis, 65°C, CO_2 loaded solution. +0.1 V 5 seconds, -1.5 V 10 minutes

Exp. 11	Pulsed electrolysis, 65°C, CO_2 loaded solution. +0.1 V 20 seconds, -1.5 V 10 minutes
Exp. 12	Pulsed electrolysis, 65°C, CO_2 loaded solution. +0.1 V 40 seconds, -1.5 V 10 minutes
Exp. 13	Pulsed electrolysis, 65°C, CO_2 loaded solution. +0.5 V 5 seconds, -1.5 V 10 minutes
Exp. 14	Pulsed electrolysis, 65°C, CO_2 loaded solution. +0.5 V 20 seconds, -1.5 V 10 minutes
Exp. 15	Pulsed electrolysis, 65°C, CO_2 loaded solution. +0.5 V 40 seconds, -1.5 V 10 minutes
Exp. 16	Pulsed electrolysis, 65°C, CO_2 loaded solution. +1.5 V 5 seconds, -1.5 V 10 minutes
Exp. 17	Pulsed electrolysis, 65°C, CO_2 loaded solution. +1.5 V 20 seconds, -1.5 V 10 minutes
Exp. 18	Pulsed electrolysis, 65°C, CO_2 loaded solution. +1.5 V 40 seconds, -1.5 V 10 minutes
Exp. 19	Constant reduction potential of -1.7 V at 65°C with **not** CO_2 loaded solution (repeat 2)
Exp. 20	Constant reduction potential of -1.7 V at 65°C with **not** CO_2 loaded solution (repeat 3)
Exp 21	Pulsed electrolysis, 65°C, CO_2 loaded solution. +1.5 V 20 seconds, -1.5 V 5 minutes

Exp. 22	Pulsed electrolysis, 65°C, CO_2 loaded solution. +1.5 V 20 seconds, -1.5 V 2.5 minutes
Exp. 23	Pulsed electrolysis, 65°C, CO_2 loaded solution. +0.1 V 20 seconds, -1.7 V 10 minutes

Appendix D - ICP Results

Table 11 presents the raw data for the ICP experiments conducted on the anolyte and catholyte of selected experiments. All data is presented in ppm and the results highlighted in yellow are far outside of the calibration range of the equipment used but are presented as illustrative only. The naming convention is that ‘Catholyte Exp. 1’ means the catholyte for experiment 1 and ‘Anolyte Exp. 1’ is the anolyte of experiment 1. The small amount of metals like chromium, potassium, and sodium are likely to be from contamination of the various chemicals and materials used in the cell, and they should not have a large effect on the results but this is not investigated in this report. The silver present is from the electrodes, possibly due to the break down of the cathode and also from the cleaning process of the silver electrodes leaving small amounts of silver particles on the surface of the electrode that are easily removed into the solution. The nickel is mostly present due to the thermocouple, while efforts were made to surround the thermocouple wires with Teflon tape this is not 100% effective at isolating it from the solution and small amounts are present in the solutions. The most interesting of the results are the concentration of Cl and SO_4 ions, these indicate how much of each of the catholyte has moved to the anode compartment and how much of the anolyte has moved into the cathode compartment. The starting concentrations of Cl in the anolyte should be close to zero, so any present in the anolyte at the end of the experiments has likely come from the cathode compartment.

Table 11 - Results of the ICP analysis for selected samples

Sample name		Concentration (ppm)										
		Ag	Al	Ca	Cr	Cu	K	Na	Ni	Cl	SO4	Si
Catholyte	Exp. 18	0,4	0	0,8	0	0	1,8	0,2	0	3792,2	6,3	0,2
Catholyte	Exp. 17	1,2	0,1	0,4	0	0	2	0,3	0,2	3479,7	20,4	0,4
Catholyte	Exp. 16	0,7	0	0,3	0	0	7,3	0,3	0,1	3844,5	15,9	0,2
Catholyte	Exp. 14	1	0	0,2	0	0	1,9	0,4	0	2696,4	11,7	0,2
Catholyte	Exp. 21	0,9	0	0,2	0	0	0,7	0,2	0,5	2955,8	9,7	0,2
Catholyte	Exp. 22	0,6	0	0,3	0	0	1	0,2	0,7	2628,6	81,5	0,2
Catholyte	Exp. 12	1	0	0,4	0	0	1,8	0,2	0,1	4152,3	15,5	0,2
Catholyte	Exp. 23	0,4	0,1	0,3	0,2	0	6,4	0,3	3,5	2852,2	29,3	0,1
Catholyte	Exp. 23	0,8	0,2	0,3	0,2	0	1,8	0,2	3,1	3144,6	17,3	0,2
Catholyte	Exp. 20	0,7	0	0,3	0,1	0,1	1,2	0,3	3,8	2817,8	9,7	0,2
Catholyte	Exp. 5	0,1	0,1	0,7	0	0	0,6	0,2	0,4	3146,1	6,3	0,1
Catholyte	Exp. 11	0,9	0	0,4	0	0	1,9	0,3	0	3516,3	13,3	0,3
Catholyte	Exp. 9	0,3	0	0,4	0	0	2	0,2	0	3080,6	10,6	0,2
Catholyte	Exp. 19	0,6	0,1	0,3	0	0	1,3	0,2	0,1	2815,8	12,8	0,2
Catholyte	Exp. 4	0	0	0,2	0	0	1,1	0,2	0,1	2660,6	7,4	0,2
Catholyte	Exp. 2	0,1	0	0,3	0	0	1,1	0,2	0,1	3565,5	7,3	0,3
Anolyte	Exp. 18	0,1	0,1	0,6	0	0	0,7	0,3	0,2	184,3	2025	0,8
Anolyte	Exp. 17	0,2	0,2	0,2	0,3	0	0,8	0,4	3,8	198,8	1548,2	0,9
Anolyte	Exp. 14	0,1	0,2	0,2	0	0	1,2	0,4	0,1	181,1	2283,3	1
Anolyte	Exp. 21	0	0,3	0,3	0,4	0,1	0,5	0,5	6,8	144,4	2357,8	1,2
Anolyte	Exp. 22	0,2	0,2	0,3	0,7	0,1	0,5	0,5	10,7	219	2215,1	1
Anolyte	Exp. 12	0,1	0,1	0,3	0,1	0	1,3	0,4	2,2	182,4	2802,7	0,9
Anolyte	Exp. 19	0	0,3	0,4	0,1	0,1	1,1	0,2	1,7	165,4	2216,8	0,5
Anolyte	Exp. 9	0	0,2	0,4	0	0	1	0,4	0,5	151,6	2116,6	1
Anolyte	Exp. 20	0	0,4	0,3	6,3	1,3	0,8	0,4	113,3	199,4	2975,2	2
Anolyte	Exp. 7	0	0,4	0,7	0,7	0	0,5	0,3	13,9	90,9	2385,9	0,3
Anolyte	Exp. 23	0	0,2	0,2	4,9	0,3	0,8	0,2	48,3	171	2390,1	0,7
Anolyte	Exp. 4	0	0,2	0,3	0	0	0,9	0,3	0,5	187	3012,8	1,3
Anolyte	Exp. 2	0,1	0,2	0,3	0	0	0,8	0,3	0,7	145,1	3084,3	1,3