REVIEW

Recent Advancement in CO₂ Capturing: An Electrochemical Approach

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Various methods have been suggested to address the problem of elevated levels of carbon dioxide (CO_2) in the atmosphere. A potential technique among these strategies is the electrochemical reduction of CO_2 (ERC), which can simultaneously solve issues like CO_2-induced global warming and enable sustainable energy storage. The ERC procedure takes place within an electrochemical cell at the interface between an ionic conductor (the electrolyte) and an electron conductor (the cathode). In this process, the anode facilitates the oxidation of water, while the cathode enables CO_2 reduction. However, a significant challenge in the ERC process lies in selecting an appropriate catalyst for the cathode material. In addition to explore the new transition metals, researchers have also investigated metal complex catalysts and nanostructures to enhance catalyst activity and product selectivity. Non-aqueous electrolytes have been employed to avoid the hydrogen evolution reaction. Ionic liquids have been proposed as a solution to address the challenge of low CO_2 solubility in the reaction medium, offering significant potential for enhancing conversion rates to resolve the limitations faced by aqueous and non-aqueous systems solid polymer electrolytes are being considered. The cell configuration has been continuously improved to improve the mass transfer effects and to better separate the reaction products. This review paper provides a preface to the ERC process and an inclusive review of several decades of research work on ERC process by analyzing the adopted various and novel cathode materials, electrolytes and cell configuration.

Keywords: Carbon dioxide, Electrochemical reduction, Catalyst, Electrodes, Electrolyte.

INTRODUCTION

Carbon dioxide (CO_2) is an important greenhouse gas as it helps to trap heat in earth's atmosphere. In the absence of CO_2, whole world would experience significantly lower temperatures. It preserves the warmness of the planet in order to provide the surviving CO_2-capturing for plants and animals as well as human. Moreover, plants use CO_2 to produce carbohydrates in the process known as photosynthesis. It is a vital naturally triggered process because all animals including human rely on plants for their food. CO_2 is generated through a range of human activities and primarily utilized by plants during the process of photosynthesis. Until last few decades, there was a balance between CO_2 emission and consumption and the CO_2 concentration was steady in the ecosystem at around 300 ppm [1-4].

Nevertheless, the imbalance between CO_2 production and consumption has been disrupted in recent decades due to the amplified anthropogenic activities, particularly the combustion of fossil fuels. This disturbance has led to a significant and concerning rise in the concentration of CO_2. According to NOAA/ESRL's Global Monitoring Division (formerly CMDL) of the National Oceanic and Atmospheric Administration, USA data in April 2015 the CO_2 global concentration was 400.72 ppm and it further increased to 404.08 ppm in April 2016. This increase in CO_2 concentrations in the atmosphere has to be significantly controlled to hold back the various undesirable alarms of climate change due to an augment in global warming. Estimates indicate that a reduction of at least 50% in CO_2 emissions is required to restrain the rise in the average global temperature to 2 ℃ by year 2050.

The current strategies employed to address the global warming crisis associated with CO_2 involve the utilization of a process known as CO_2 sequestration. This process is commonly referred to as carbon dioxide capturing and storage (CCS) [1,3]. CCS techniques are firstly capturing CO_2 from concentrated

point sources, for instance from fossil fuel power plants. Secondly, bringing it to a storage site and dumping it where it will not escape to the atmosphere such as underground geological formation. Common carbon capturing options available are: (i) post-conversion (ii) pre-conversion (iii) oxy-fuel combustion. In post-conversion capture, the CO_2 separation process takes place after the carbon source has been converted into CO_2, such as in the treatment of flue gas from industrial processes. Pre-conversion capture involves capturing CO_2 as an unintended byproduct during an intermediate reaction within a conversion process. This can occur in various industrial processes, such as the production of ammonia or coal gasification in power plants. On the other hand, oxy-fuel combustion is a method where pure oxygen is employed as the main oxidant in a combustion process. The fuel has been burnt with pure oxygen as a replacement for air, hence no CO_2 emission. These CO_2 capturing options are extensively investigated by researchers over several years and reviewed by several authors [1,4-13]. Among the choices at hand, post-combustion capture encompasses established methods for CO_2 separation, such as chemical solvent absorption, solid sorbent adsorption, membrane separation and cryogenic separation. Table-1 listed the advantages and disadvantages associated with the CO_2 capture technologies that have been utilized.

In CO_2 mitigating research field, CCS has gained recognition as a promising and advanced field of research. However, its economic feasibility and life cycle assessment still need to be determined, despite some previous efforts in this regard. One significant concern with CCS is the safe and long-term storage of captured CO_2. Incidents like the "Lake Nyos" disaster, where CO_2 leaked from a naturally occurring sequestration site and resulted in the loss of 1,700 lives, have raised concerns about its environmental impact [14]. Therefore, it is crucial not only to sequester carbon dioxide but also to explore its utilization by converting it into valuable products.

In recent times, a closely related alternative known as carbon capture and utilization (CCU) has gained significant global attention. This strategy aims to convert CO_2 waste into useful substances, such as chemicals and fuels, while simultaneously supporting initiatives to address climate change. Options for utilizing waste CO_2 encompass various approaches, including direct utilization, enhanced recovery of oil and coal bed methane, conversion of CO_2 into chemicals and fuels and mineral carbonation [1,4]. In recent times, there has been significant research focus on transforming CO_2 into chemicals and fuels among these alternative options. Numerous methods have been proposed for this conversion, including radiochemical, thermochemical, hydrogenation, methane reforming, photochemical, electrochemical, biochemical and photoelectrochemical methods [15].

Among the various processes discussed, electrochemical reduction of CO_2 (ERC) stands out due to its numerous advantages, particularly when electricity is sourced from renewable energy. One significant advantage of ERC is its ability to operate under ambient temperature and pressure conditions. Additionally, ERC benefits from utilizing water as a readily available and cost-effective source of hydrogen ions. One of the benefits of ERC is its flexibility in generating various products from the same source materials, CO_2 and water, through the adjustment of the electrode system and electrochemical conditions. As a result, ERC has garnered significant attention from the scientific community, leading to the publication of several review papers on the topic [15-25]. The scope of this review paper is to provide a preface of ERC and to focus on the recent advancements in ERC process.

Preface of electrochemical reduction of CO_2: The electrochemical reduction of CO_2 (ERC) refers to the process of utilizing electrical energy to convert CO_2 into more useful chemicals, specifically focusing on the production of "CO_2 neutral fuels". In 1957, Teeter *et al.* [26] proved the ERC to formate at mercury electrode (cathode). In 1985, Hori *et al.* [27] made a significant finding in the field of electrochemical reduction of CO_2 (ERC). They observed that CO_2 may be directly converted into hydrocarbons with a satisfactory level of current density and current efficiency when using a copper foil electrode. Since then ERC has garnered significant attention within the field of applied electrochemistry, resulting in an extensive collection of research articles and a multitude of patents.
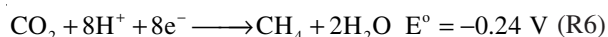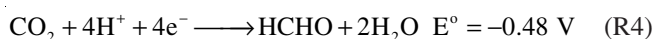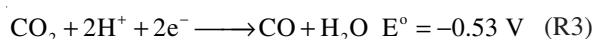
| | TABLE-1 | |
| | COMPARISON OF CO_2 CAPTURE TECHNOLOGIES | |
Process	Advantages	Disadvantages
Absorption by chemical solvents	• Experienced and extensively used technology for efficient percentile capture of acid gases	• Not cost-effective as high partial pressure is required when using physical absorbents • The extended duration is necessary due to the requirement of low pressure when employing chemical solvents
Adsorption by solid sorbents	• Hundred percent purity of products can be attained • When equipment size turns into a concern simplicity in adsorbent relocation to remote fields	• Lower product recovery • Comparatively sole pure product
Membrane separation	• Ease and low capital investment • Steadiness at high pressure • Elevated product recovery • Less weight and space efficiency • A lesser amount of environmental impact	• Permeate recompression • Hot high purity
Cryogenic separation	• Enhanced recovery compared to various other processes • Product purity is high	• Regeneration is ineffective • Small size scale down is not economical

ERC into chemicals (CO_2 neutral fuels) occurring in an electrochemical cell (mostly liquid phase partitioned cell divided by an ion exchange membrane) at the interface of an electron conductor (cathode) and an ionic conductor (electrolyte) (Fig. 1). General electrochemical reaction occurring at cathode (reduction reaction) is:

$$CO_2 + xe^{-1} + xH^+ \xrightarrow{\text{eV}} \text{Hydrocarbons} \qquad (R1)$$
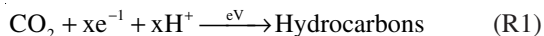
The reduction of carbon dioxide through electrochemical processes yields a diverse range of hydrocarbons, encompassing both liquid and gaseous products. Formic acid, methanol, ethanol and propanol are among the liquid products generated, while the gaseous products include methane, ethane and syngas. These reactions typically occur under neutral pH conditions and at room temperature, with reference to the standard hydrogen electrode (SHE) [21]:

$$CO_2 + H^+ + 2e^- \longrightarrow HCOOH \quad E^\circ = -0.61 \text{ V} \qquad (R2)$$

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O \quad E^\circ = -0.53 \text{ V} \qquad (R3)$$

$$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + 2H_2O \quad E^\circ = -0.48 \text{ V} \qquad (R4)$$

$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O \quad E^\circ = -0.38 \text{ V} \qquad (R5)$$

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O \quad E^\circ = -0.24 \text{ V} \qquad (R6)$$

The protons required for the reduction reactions (R2-R6) at the cathode are supplied by the oxygen evolution reaction (R7) *i.e.* by water oxidation at the anode.

$$nH_2O \longrightarrow nO_2 + 4nH^+ + 4ne^- \qquad (R7)$$

Hence in total the overall transformation occurring in the electrochemical device (Fig. 1) is:

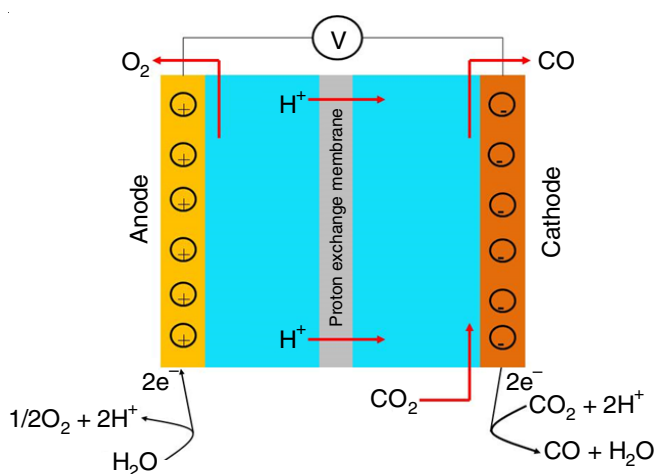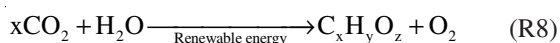$$xCO_2 + H_2O \xrightarrow[\text{Renewable energy}]{} C_xH_yO_z + O_2 \qquad (R8)$$

Fig. 1. Electrochemical cell for CO_2 reduction

This ERC is expanding notable consideration among the scientific community as CO_2 mitigation technique because this uses CO_2 and inexpensive water as raw materials to produce various useful chemicals and byproduct is another useful element *i.e.*, oxygen. Hence, the reduction and transformation of wasted CO_2 into valuable chemical feedstock aligns the ERC process with the principles of sustainable chemistry. However, a significant amount of electrical energy is needed for cathode reaction (R1) to proceed forward and this energy ultimately converted to energy stored in the chemical bonds of the compounds produced. Using electricity generated from burning fossil fuels does not contribute to the mitigation of atmospheric CO_2 concentration and does not align with the ultimate goal of CO_2 mitigation. To effectively reduce the net CO_2 concentration in the atmosphere, it is essential to source electricity from carbon-free renewable energy sources. By this way, renewable energy can be stored efficiently as chemical energy in the produced chemical feed stock. Hence, the significant concern regarding the disparity between energy generation and consumption, especially in the context of renewable energy sources that depend on natural factors for their efficiency, can be resolved. This is a spectacular added advantage of ERC scenario.

Electrochemical cell and mechanism: From all the published reviewed articles, it can be observed until now there is neither any standard cell configuration nor experimental setup methodology for use in ERC experiments. Different research group utilized a different type of electrochemical cell. Numerous researchers have expressed the belief that while cell configuration may influence mass transport, it does not serve as the limiting factor in the ERC process. Therefore, it is feasible to compare results across different cell configurations and experimental methodologies [16,24]. Traditionally undivided three-compartment electrochemical cells used for ERC and even some recent researches were done by using these type of cell [28-30]. This has the drawback of re-oxidation of reduced products at the anode. So commonly used cell configuration is, divided two-compartment electrochemical cell. Either a proton exchange membrane, agar bridge or glass frit are used to partition the cathode and anode compartments [31-37]. Some researchers adopted H-type electrochemical cell to separate anode and cathode and utilized the ion exchange membrane to enhance proton transfer [38-40]. The configuration of the electrochemical cell has been continuously improved to facilitate the ERC experiment. Kuhl *et al.* [41], designed a cell to optimize the product concentrations and for the direct classification and quantification of liquid and gas products by coupling the cell to gas chromatography and nuclear magnetic resonance. What-ever the configuration, the essential components of electro-chemical cells are electrode and electrolyte. Electrode should catalyze the ERC and electrolyte should act as a reaction medium. A comprehensive examination of numerous categories of electrodes and electrolytes has been conducted, and a thorough analysis of these investigations is presented in the subsequent sections.

The complete mechanisms of ERC which include mass transfer, adsorption and reaction have been proposed by a number of researchers in different ways. Because the reaction pathways and resulting product distribution depend on so many inherent factors such type of electrode, electrolyte and cathode potential. Fig. 2 shows the commonly proposed scheme for ERC.

The first phase of electrochemical reduction of CO_2 (ERC) involves the adsorption of carbon dioxide molecules onto the surface of the electrode, specifically the cathode. Most of the work on ERC focused on the conversion of CO_2 that absorbed into water or some other solvents. So before adsorbed into
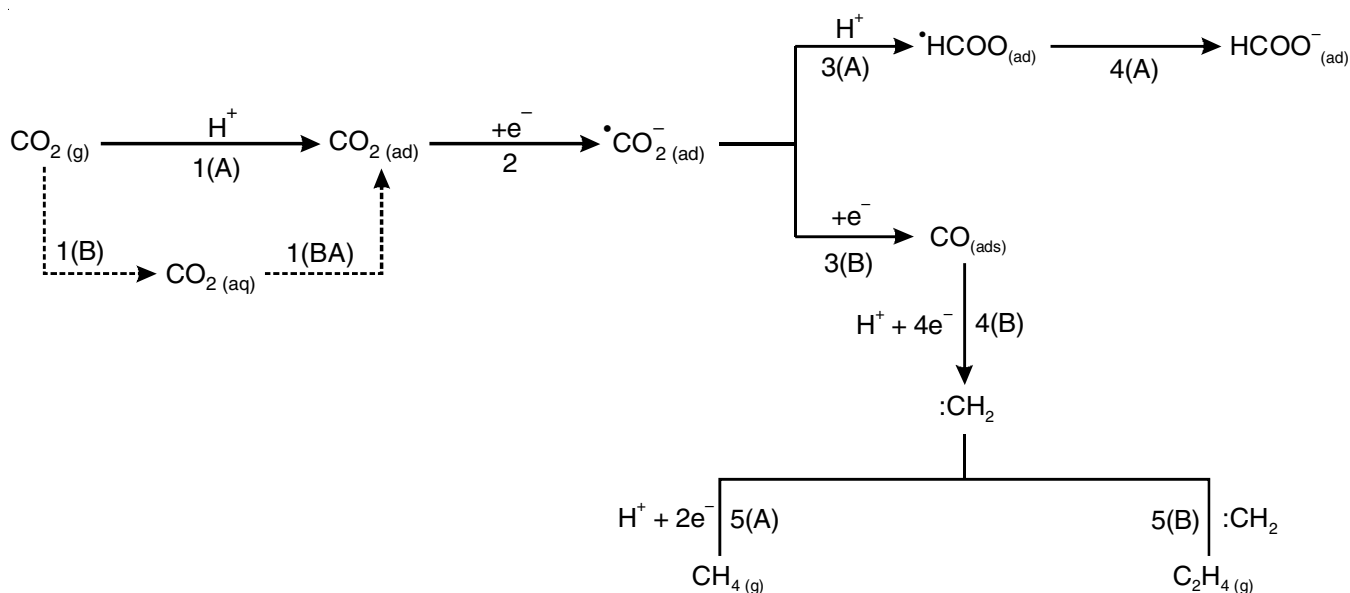
Fig. 2. Commonly proposed scheme for electrochemical reduction of CO_2

electrode the hydration step 1(B) is necessary which may have great influence in the overall process efficiency because of the solubility of the solvent determines the availability of $CO_{2(aq)}$ and thus controls the $CO_{2(ad)}$ concentration at the cathode interface. Particularly when chemical CO_2 adsorption occurs without physical absorption this result in available free CO_2 for conversion and chemical adsorption have to be reversed for release free CO_2. This stripping it self-energy consuming and limits the overall process efficiency. Therefore, more work focusing converting CO_2 from gas phase rather than liquid phase. Once CO_2 is adsorbed onto the electrode, it undergoes a conversion into an intermediate radical called $^{\bullet}CO_2$. This radical possesses a standard redox potential of approximately -1.9 V (SHE). Despite its high energy state, this intermediate radical $^{\bullet}CO_2$ only serves to kinetically hinder the ERC process. Nevertheless, it is important to highlight that the overall standard redox potentials for the ERC and the reduction of protons to hydrogen gas (with a standard potential of zero volts *versus* the standard hydrogen electrode) exhibit comparable ranges. From these intermediate radicals depend on the ERC conditions and the proton and electron transfer various end products can be formed as listed in Fig. 2. The overall ERC performance of an electrochemical cell is characterized by its faradic efficiency, current density, overall potential and energy efficiency.

Faradaic efficiency (FE): Faradaic efficiency or current efficiency, quantifies the portion of electric current within the cell that directly contributes to the generation of the desired product. This is determined by dividing the charge employed for producing the specific product by the total charge passed through the cell during the ERC process [24]. The Faradaic efficiency for given product can be calculated using eqn. 1:

$$\varepsilon_{Faradaic} = \frac{z.n.F}{Q} \tag{1}$$

In the given context, the variable 'z' represents the number of electrons involved in reactions R2 to R6. For example, z equals 2 for CO in reaction R3. The variable 'n' corresponds to the number of moles of a specific product; 'F' denotes Faraday's constant, which has a value of 96485 C/mol. Lastly, 'Q' represents the total charge that has traversed through the cell during the experiment.

Current density: Current density refers to the magnitude of the electric current at a specific cell potential, divided by the active geometric surface area of the cathode. It serves as a metric for assessing the rate of electrochemical reactions, analogous to the rate of heterogeneous reactions in conventional catalytic systems. By evaluating the current density, it becomes possible to determine the required electrode area and the size of the electrochemical cell.

Overpotential: In an ideal system, the reduction of carbon dioxide should occur at a specific metal electrode, precisely at the thermodynamic potential as described in the previous equations. However, in practical applications, a more negative potential is typically necessary to drive the reaction, which is known as the overpotential. The overpotential represents the additional potential required to facilitate the reaction. It is important to observe that higher overpotential values indicate a greater amount of energy needed to carry out the desired reaction.

Energy efficiency: The energy efficiency is defined as:

$$\varepsilon_{energetic} = \Sigma_k \frac{E_k^o \varepsilon_{k,Faradaic}}{E_k^o + \eta} \tag{2}$$

In this context, E_k^o refers to the equilibrium cell potential associated with a specific product; $\varepsilon_{k,Faradaic}$ represents the faradaic efficiency of product 'k' while 'η' denotes the cell overpotential. It is important to understand that high Faradaic efficiency and a low overpotential would result in a substantial enhancement of energy efficiency.

The overall performance of an electrochemical cell for CO_2 reduction is influenced by several factors, including the type of metal electrode, the characteristics of the electrolyte and various reaction parameters such as pH, potential, tempera-

ture and pressure. The following sections provide a comprehensive review of the impact of these parameters on the CO_2 reduction process.

Electrodes: Because of the inherent stability of **s** as a molecule, a significant amount of energy is required to break it apart. Nevertheless, by employing an appropriate catalyst as a cathode in the electrochemical cell for ERC, the energy demand can be significantly decreased. Moreover, the selection of appropriate catalyst can improve the energy efficiency of ERC process and control other important parameters such as product selectivity and production rates. The key points in ERC process are successive CO_2 adsorption on to electrode, intermediate formation and product formation and removal from the active sites of the electrode. Numerous theoretical and kinetics studies have extensively investigated ERC and have established that the process's performance is heavily influenced by the binding energy of the crucial intermediate involved in the reduction of CO_2 on electrode, which is commonly believed to be CO [15,42,43]. Elements that exhibit strong binding with CO tend to generate fewer products in the CO_2 reduction process. This is primarily due to the poisoning effect caused by CO or other intermediates, which hinders the formation of desired products, particularly hydrogen derived from competing water reduction. In contrast, elements that display weak binding with CO_2 predominantly produce CO as a product. When CO_2 is reduced to CO, the CO molecule is released from the surface rather than participating in the formation of further reduced products like alcohols and hydrocarbons. In order to achieve the optimal binding energy of CO, it is necessary to utilize elements that possess intermediate binding energy. Hori *et al.* [27] discovered that transition metals exhibit significant potential as electrode materials in the electrochemical reduction of CO (ERC) process. This is primarily attributed to the vacant orbitals and active *d*-electrons present in transition metals. The unique characteristics of transition metals allow them to energetically strengthen the bonding between the electrode and CO_2 during the process of product formation. This enhanced bonding facilitates the desorption of the reduction products from the electrode surface [18,22,43-46]. The investigation of ERC has involved comprehensive research on transition metals and their compounds.

Azuma & Watanbe [47] conducted a study on ERC using 32 different metal electrodes in an aqueous electrolyte under ambient conditions. Similarly, Hara *et al.* [48] explored ERC under high pressure conditions. Out of 32 metals, only Cu was able to produce hydrocarbon efficiently and showed high total current efficacy for CO_2 reduction. In the periodic table, the IIB, IIIB and IVB group heavy transition metals reduced CO_2 to formate, while VIII IB group metals reduced CO_2 to CO. Copper demonstrates an intermediate position between these two groups and displays selective activity in facilitating the reduction of CO_2 to hydrocarbons.

Several studies have conducted comparisons on the performance of various transition metals for ERC catalysis. However, none of these pure metals investigated thus far exhibit sufficient activity to be commercially viable. An ideal catalyst for ERC would function at high current density and low overpotential,

enabling selective production of the desired product. Consequently, research efforts have shifted towards exploring novel metals and enhancing the performance of existing metal electrodes using different techniques. Various types of electrocatalysts are commonly employed in the literature for different applications for example (i) bulk metal; (ii) metal oxides; (iii) metal complexes; and (iv) modified metals.

(i) Bulk metal: Different pure metals have been studied by researchers as cathode material for ERC and among this copper (Cu) is one of an ideal metal for obtaining more desired product *i.e.*, hydrocarbons and alcohols. Gattrell *et al.* [20] presented an in-depth analysis on the reduction of CO_2 at Cu electrodes in aqueous electrolytes. Intermediate hydrogen overvoltage and a weak CO adsorption are the advantages of copper electrodes. Therefore, it is catalyzed carbon-oxygen bond breaking in CO_2 and desorbs the CO. Further at Cu electrodes, CO reacts to more reduced products in significant amounts at low current efficiencies. Hence, Cu as a metal electrode has been extensively studied by many researchers [30,38,49-58]. However, Cu as electrode metal is still a topic of debate because of its high attraction for absorbed oxygen, since the affinity for absorbed oxygen makes organic compounds to easily contaminate the Cu metal electrode surface. Kaneco *et al.* [49] in 1999 conducted an investigation on the ERC using a copper electrode. In this study, a methanol-based electrolyte containing potassium supporting salts was utilized at low temperature. The electrochemical reduction of CO_2 resulted in the production of several main products, including methane, ethylene, ethane, carbon monoxide and formic acid. In 2020, Firet *et al.* [58] presented a methodology for conducting X-ray absorption spectroscopy (XAS) experiments on an electrochemical cell that carried out CO_2 reduction. The study specifically focused on utilizing copper and silver gas diffusion electrodes.

As it is believed next to Cu, silver (Ag) has low activity for the HER and possesses fairly weak CO adsorption, Ag also studied by researchers as a metal electrode for ERC [59-63]. Under ambient conditions, Hatsukade *et al.* [59] examined the activity and selectivity of ERC on metallic silver surfaces, observing a total of six reduction products. The major products were CO and hydrogen, while formate, methane, methanol and ethanol were observed as minor products. In 2018, Jeanty *et al.* [63] demonstrated the feasibility of long-term electrolysis of CO_2 to CO using a Ag GDE in the flow-by operation mode. The process operated at a current density of 150 mA cm^{-2} for several hundred hours. The Faradaic efficiency for CO (FECO) was observed to be approximately 60% on a 100 cm^2 electrode area.

Several other transition and noble metals like platinum were also studied for ERC process [36,64-67]. The majority of studies reached a consensus that a form of reduced CO_2 is present, although varying opinions exist on the specific nature of the reduction. Hoshi *et al.* [67,68] found that differing from other Pt group metals, Pd electrode surface has the highest activity. However, poisoning the adsorbates are a negative aspect of the Pd electrodes [69,70]. Podlovchenko *et al.* [71] observed the electroreduction of CO on dispersed electrolytic deposits of palladium. Interestingly, this reduction occurred at potentials that were more positive than the reversible

hydrogen potential (RHP). In their study, Summers *et al.* [28] employed molybdenum (Mo) as an electrode and demonstrated its capability to convert CO_2 into methanol. One of the drawbacks associated with the Mo electrodes is their susceptibility to corrosion under open circuit conditions.

In 2018, Natsui *et al.* [72] investigated the electrochemical reduction of CO_2 to formic acid (HCOOH) using boron-doped diamond (BDD) electrodes in a flow cell setup. The BDD electrodes were chosen due to their superior electrochemical properties compared to metal electrodes, as well as their high durability. The study reported a remarkable faradaic efficiency of 94.7% for the production of HCOOH. Similarly, Lee *et al.* [73] investigated the ERC using a membrane electrode assembly comprising a GDE and an anion exchange membrane (AEM). They tested different metal powders including Pd, Ag, Zn, Cu, Sn, Ru, Pt and Ni as cathode catalysts. Among these, Pd and Ag exhibited high current density and Faradaic efficiency for CO production, while maintaining a low cell resistance. Wu *et al.* [74], in 2013, employed Sn GDE for the converting CO_2 into formate, similarly, In 2019, Li *et al.* [75] conducted a study on a porous Sn electrode with adjustable pore structure, proposing its potential as a promising candidate for the reduction of CO_2 to formate.

In their study published in 2020, Zhang *et al.* [76] conducted an experiment aiming to investigate a method for altering the catalytic properties of a metallic Pd catalyst by applying a surface coating of polydiallyldimethyl ammonium (PDDA) polymer. The resulting catalyst, PDDA-functionalized Pd/C catalysts, exhibited improved CO Faradaic efficiency of approximately 93% and achieved a current density of 300 mA cm^{-2} at a potential of -0.65 V *versus* the reversible hydrogen electrode. Lim *et al.* [77] conducted an experiment aiming to develop an improved catalyst for the ERC. They prepared Sn electrocatalysts with dense tips, which proved to be effective in producing formate through ERC with a high productivity. The catalyst demonstrated a Faradic efficiency of 62.5% and a partial current density of -18.7 mA cm^{-2} in a neutral electrolyte. Furthermore, Yang *et al.* [78] investigated the role of carbon GDLs and applied potential on flooding during ERC. The researchers utilized various GDEs such as Ag deposited on a carbon-GDL and Ag deposited on a PTFE membrane. Electrochemical impedance spectroscopy (EIS) measurements were conducted for each GDE in a CO_2 atmosphere with $KHCO_3$ serving as electrolyte. It was observed that the high negative potentials required for driving ERC caused adjusting in the wetting properties of the carbon-based GDL.

(ii) Metal oxides: The studies reported rather than pure bulk metals, metal oxides reveal much better results in ERC experiments. In 2012, Li *et al.* [79] reported reducing the thickness of Cu_2O films caused the low overpotential CO_2 reduction on Cu electrodes and they found under identical conditions. The stability of the polycrystalline Cu electrode lasted for only 1 h, whereas the modified electrodes remained stable for several hours. The deposition of copper oxide layers on the electrode's surfaces are well documented because to its capability to reduce CO_2 to methanol [30,31,55]. Chen *et al.* [80] studied enhanced activity of Sn/SnO_2 thin film catalysts for CO_2 reduction. Rather

than tin electrode the electrode with a native tin oxide layer revealed an elevated level of partial current density and enhanced efficiency for the reduction of CO_2. Their results implicated the CO_2 reduction pathway have been positively influenced by the participation of tin oxide on tin electrodes. Metal/metal oxide composite materials offer assuring prospects as catalysts for environmentally-friendly fuel production through the ERC process.

Aqueous CO_2 reduction on oxide derived gold (Au) nanoparticles at very low overpotential were reported by Chen *et al.* [37]. According to their results, the oxide-derived Au nanoparticles maintained their catalytic activity for 8 h and exhibited a remarkable selectivity for the reduction of CO_2 to CO in water, even at low overpotentials of 140 mV. Conversely, Noda *et al.* [81] independent titanium (Ti) electrodes demonstrated limited catalytic effectiveness for the ERC process. In contrast, titanium oxide (TiO_2) shows promise as a catalyst for the ERC process. It has been utilized in combination with additional metal oxides that are deposited onto titanium (Ti) substrates to enable the ERC [79-82].

(iii) Metal complexes: Several metal complexes have also been reported to be able to catalyze the ERC [47,83-94]. Varela *et al.* [89] synthesized a dinuclear copper complex that demonstrated an inherent ability to capture and reduce CO_2. Remarkably, this complex exhibited CO_2 reduction even at applied potentials as low as -0.03 V *vs.* SHE. In 1974, Meshitsuka *et al.* [95] conducted pioneer research by employing a dip-coated graphite electrode coated with nickel or cobalt phthalocyanine for catalyzing the ERC. Verdejo *et al.* [96] showed copper complexes able to fixate CO_2 directly from the air. By utilizing nickel cyclams, precise electrochemical conversion of CO_2 to CO with high selectivity has been achieved under aqueous conditions. Additionally, copper complexes were observed to form bridges between two CO_2 molecules, resulting in the formation of oxalate, which could be extracted using a lithium salt. Balazs *et al.* [97] studied the electrocatalytic activity of $Ni(cyclam)^{2+}$ for ERC. The exceptional electrocatalytic activity of $Ni(cyclam)^{2+}$ complex for CO_2 reduction can be attributed to the formation of the strongly adsorbed $Ni(cyclam)^{+}$ complex through reductive adsorption on mercury electrodes. The catalytic activity of the catalyst was significantly reduced in the presence of CO at unstirred mercury electrodes. This limitation poses challenges to the long-term effectiveness of the catalyst since CO is the primary product resulting from the reduction of CO_2. The carbine-pyridine nickel complexes were employed for the ERC in aqueous solutions. The reduction process occurred at applied potentials ranging from -0.86 to -1.54.V [97] and exhibit the exceptional selectivity in the conversion of CO_2 to CO. However, the production of CO was only moderate and the catalyst exhibited deactivation when continuously operated at high applied potentials. When dinickel macrocyclic complexes were utilized for CO_2 reduction at approximately -1.00 V *vs.* SHE, the reduction resulted in the formation of CO and carbonates, with only small quantities of formate observed [98].

Cobalt based complexes are also being studied for their potential to enhance catalytic activity in ERC studies by several

researchers [88,99-109]. When Co phthalocyanin coated on a carbon electrode formate was the main product with small amounts of methanol [104], while CO is the major product of ERC in water, when using Co macrocycles [105]. Shen *et al.* [90], reported new approaches in the ERC facilitated by a fixed or immobilized catalyst Co protoporphyrin. In comparison to the most advanced electrocatalysts based on porphyrin reported in the literature, the immobilized cobalt protoporphyrin on a pyrolytic graphite electrode demonstrated superior efficiency and selectivity in the reduction of CO_2. This reduction occurred at relatively low overpotentials in an aqueous acidic solution. In 2016, Kramer *et al.* [91] used customized electrodes with cobalt phthalocyanine (CoPc) and immobilized in a poly-4-vinylpridine (P4VP) film. Comparing to those customized with CoPc alone, cobalt phthalocyanine (CoPc) immobilized in a poly-4-vinylpridine (P_4VP) film electrode revealed significantly improved and selectivity. Lin *et al.* [105] reported covalent organic frameworks (COFs) modular optimization. In covalent organic frameworks (COFs), the building units are cobalt porphyrin catalysts coupled by organic struts through imine bonds. The COFs at pH 7 revealed the Faraday efficiency (FE) of 90% and turnover numbers up to 290,000 with an overpotential of –0.55 V. In comparison with the molecular cobalt complex this is 26-fold step up in activity and for 24 h no degradation was recorded. In a study conducted by Abdinejad *et al.* [109], it was reported that metalloporphyrin complexes; cobalt and iron porphyrins, such as CoP and FeP, demonstrate significant potential as electrocatalysts for CO_2 reduction, showing promising prospects.

In 2019, Wang *et al.* [110] demonstrated that cobalt phthalocyanine (CoPc2) exhibits a remarkable selectivity for the conversion of CO_2 to CO across a wide range of pH values. This selectivity was maintained consistently from acidic (pH 4) to basic solutions (pH 14). The researchers achieved an average selectivity of 92% for CO_2 reduction, along with partial current densities of 20 mA cm^{-2} at the cathode. Importantly, the CoPc2 catalyst exhibited excellent stability over time in the entire pH range studied.

Palladium based complexes also studied by few researchers [111-113]. During anhydrous conditions, if monodentate palladium complexes were used the CO_2 reduction begins at about -1.30 V. In the existence of water within the electrolyte, the presence of hydrogen and formic acid was observed, while the detection of CO production was absent [114]. Nevertheless, it was discovered that by increasing the donor strength of the ligands, the production of CO could be enhanced while reducing the formation of formic acid. Palladium complexes featuring pyridine and pyrazole ligands exhibited electron acceptor properties at appropriate potentials. This increased the donor strength of the ligands and consequently influenced the selectivity of products during the ERC process. Walsh *et al.* [115] recently conducted investigations on enhancing the efficiency of ERC through the use of immobilized manganese complexes. Eventually, any modified metal complex has its advantages and disadvantages in the overall performance of ERC process. According to the recommendations of Benson *et al.* [116], in order to obtain an outstanding selectivity for desired products

like methanol in the ERC process, it is crucial to utilize specific catalysts at specific stages. The catalysts contribute significantly in regulating the reaction pathways and facilitating the formation of the desired products. Through meticulous selection and design of catalysts, it becomes feasible to enhance the efficacy and selectivity of the ERC process, directing it towards the desired product, such as methanol.

In 2019, Yuan *et al.* [117] introduced a method for doping N-C materials with single dispersed Ni atoms to enhance the performance of CO_2 reduction reaction (CO_2RR). They utilized a unique metal-organic complex precursor to derive Ni-N-C nanosheets, which served as a single-atom catalyst. Compared to a pure N-C sample, the Ni-N-C catalyst demonstrated significantly improved CO_2 conversion performance. Significantly, it demonstrated an impressive Faradaic efficiency of around 91.2% for CO production. In 2019, Dai *et al.* [118] synthesized bimetallic oxide catalysts, specifically Bi_2O_3-CuO(x), using a coordination-precipitation method with precise control over atomic ratios (Cu/Bi). These catalysts exhibited remarkable performance in effectively reducing CO_2 to formate, achieving a maximum Faradaic efficiency of 89.3% at a potential of -1.4 V *vs*. SCE. Furthermore, the catalyst demonstrated robustness during 10 h of continuous electrolysis. In another study, in an aqueous environment, a novel class of CO_2 reduction catalysts was introduced [119], which involved the use of graphitic carbon nitride (g-C_3N_4) embedded with transition metals. The researchers found that bimetallic catalysts, specifically (NiMn or NiCu)-C_3N_4, exhibited higher efficiency compared to catalysts containing a single metal. The improved performance was ascribed to the synergistic effects arising from the coexistence of two transition metals. The catalyst structure, incorporating both nickel and manganese or nickel and copper, exhibited increased catalytic activity for the reduction of CO_2.

In 2020, Dutta *et al.* [120] conducted a study on bimetallic AgCu foam electrocatalysts for the production of ethanol from CO_2 through selective Cu oxidation and reduction. The catalyst demonstrated selectivity towards CO at low overpotentials, while at high overpotentials, it exhibited selectivity towards C_2H_4 (ethylene). The bimetallic AgCu foam electrocatalysts showed the ability to control the desired product by selectively promoting either CO formation or C_2H_4 formation depending on the applied overpotential. Catalyst for selective ethanol formation was obtained by thermal annealing of $Ag_{15}Cu_{85}$. Zhang *et al.* [121] investigated high-current performance for the CO_2RR electrolyzer. They designed nickel phthalocyanines on carbon nanotubes as molecularly dispersed electrocatalysts to fabricate gas-diffusion electrodes. Recently, Tsubonouchi *et al.* [122] synthesized newly Co complex, [Co^{II}(bibpy)L] (1-L, L is an axial ligand) with an equatorial N 4 ligand of bibpy 2 –(H_2bibpy = 6,6′-*bis*-(1*H*-benzimidazol-2-yl)-2,2′-bipyridine) to study electrocatalytic CO_2 reduction in a homogeneous DMF medium.

(iv) Modified metals: Researchers experienced the electrode particles size involved in ERC have great influence on Faraday efficiency, energy efficiency and product selectivity [44,115,116,123-129]. Advancements in nanoparticle synthesis techniques have enabled the study of the impact of controlled surface area and surface morphology on enhanced

reaction kinetics. These developments have provided opportunities to explore how specific characteristics of nanoparticles, such as their surface area and morphology, can influence the rate of chemical reactions. The outstanding electrocatalytic activity for CO_2 reduction to formate was observed in high surface area SnO_2 nanocrystals synthesized through a simple hydrothermal method. These nanocrystals exhibited remarkable performance at overpotentials as low as approximately 340 mV [126]. The concession between the robust interaction between $CO_2^{\bullet-}$ and the nanoscale tin surface, along with the resulting enhanced activation of kinetics for protonation and additional reduction, leads to this notable reactivity in CO_2 reduction. Kim *et al.* [130] constructed a engineered platform consisting of ordered monolayers to investigate the crucial catalytic activity of carbon dioxide reduction. This was achieved by utilizing gold-copper bimetallic nanoparticles with varying compositions. The nanoparticle monolayers exhibited superior performance as catalysts in the ERC process.

Zhu *et al.* [131] investigated monodisperse Au NPs for selective electrocatalytic reduction of CO_2 to CO. The 8 nm Au NPs exhibited the maximum Faraday efficiency up to 90% at –0.67 V *vs*. RHE among the various monodisperse nanoparticles tested. The potential of monodisperse Au NPs accomplished both efficient and selective electrocatalytic reduction of CO_2 to CO. By optimizing the binding sites of the existing reaction intermediates, the capability of Au NPs to achieve high selectivity for CO through the formation of thick Au oxide films is demonstrated. These Au NPs exhibited a remarkable selectivity towards CO even at low overpotentials of 140 mV in ERC experiments conducted in a 0.5 M $NaHCO_3$ solution. Moreover, these thick Au oxide films obtained Au NPs have retained their activity for at least 8 h [38]. Recently, oxide derived Cu NPs gained significant attention due to its outstanding performance in ERC experiments [132,133]. In their study, Gao *et al.* [134] investigated selectivity variation based on the size of CO_2 in ERC experiments using Pd NPs with sizes ranging from 2.4 to 10.3 nm. As the nanoparticle size reduced from 10.3 to 3.7 nm, there was an 18.4-fold increase in the current density and a corresponding variation in the Faradaic efficiency for CO production was observed.

Generally, the good quality electrocatalyst is a precious metal such as Pt and Au. Therefore, supporting the expensive electrocatalyst on a conductive substrate is advantageous as it allows for high dispersion of the catalyst, thereby reducing the amount of precious metal required without compromising catalytic activity [25,135-141]. Among the different types of supports, carbon materials such as graphite nanofibers (GNF) and carbon nanotubes (CNTs) attract a growing interest due to their fascinating and useful properties. Gangeri *et al.* [137] studied the usage of Pt/CNT and Fe/CNT as electrocatalysts in ERC experiments to convert CO_2 to liquid fuels, mainly to isopropanol. Despite the observation of faster deactivation, the Fe/CNT catalyst exhibited improved behaviour compared to Pt/CNT. Kang *et al.* [135] employed a non-covalent binding strategy to immobilize an iridium pincer dihydride catalyst on carbon nanotube-coated gas diffusion electrodes (GDEs). The prepared GDEs were proficient, selective, long-lasting, gas

permeable electrodes engineered for electrocatalytic reduction of CO_2 to formate.

Sen *et al.* [142] analyzed the catalytic characteristics of Sn and SnO_2 nanoparticles deposited on gas diffusion layers (GDLs) for the purpose of electrochemically reducing carbon dioxide to formate. The researchers assessed the efficiency and long-term stability of these electrodes in a gas-fed electrolysis cell, where a liquid electrolyte stream was continuously flowing. Furthermore, they incorporated an integrated reference electrode into their experimental setup. On the other hand, Huang *et al.* [143] developed a top-down approach involving multiple-redox treatment to achieve downsized copper crystals on self-supported copper electrodes. This innovative method aimed to enhance the selective electroreduction of CO_2.

In 2020, Abdinejad *et al.* [144] demonstrated the effectiveness of copper electrodes, which significantly enhanced the current density compared to glassy carbon electrodes when ethylenediamine (EDA) was used as the catalyst. Additionally, the Faradaic efficiency was greatly increased from 2.3% to 58%. Castelo-Quibéna *et al.* [145] synthesized different types of carbon gels doped with iron as cathodes for the electrocatalytic reduction of CO_2 under atmospheric pressure conditions. The materials investigated included an aerogel, three xerogels with varying iron components and a composite consisting of carbon xerogel and carbon nanofibers. All of these electrocatalysts exhibited enhanced formation of C1 to C4 hydrocarbons, with a notable emphasis on the selectivity for C3 hydrocarbons within this group. In a study conducted in 2019, Wang *et al.* [146] analyzed the influence of copper nanoparticle morphology on the electrocatalytic activity of CO_2 reduction using GDEs and alkaline catholytes with a continuous flow.

In 2020, Hou *et al.* [147] successfully prepared atomically dispersed Ni-N species in hierarchically porous nitrogen-doped carbon nanotubes (NCTs) through a self-sacrifice template approach involving the pyrolysis of ZnO@ZIF-NiZn core-shell nanorods. The resulting Ni/NCTs-50 catalyst exhibited nearly 100% CO Faradaic efficiency over a wide potential range, from -0.6 V to -1.0 V. Similarly, in the same year, Ma *et al.* [148] proposed ultrathin Ni and nitrogen-codoped carbon nanosheets (Ni-N-CNSs) through a facile *in situ* pyrolytic strategy. The nanosheets exhibited an extremely thin and porous structure, offering a significantly expanded surface area, ample mesoporous volume and evenly distributed Ni atoms. The optimized catalyst demonstrated a high CO Faradaic efficiency of nearly 100%, a partial current density of 121.4 mA mg^{-1}, a CO production rate of 37.7 μmol mg^{-1} min^{-1} and exceptional durability. A typical metal/C electrode consisting of an Au/C nanoparticle film immobilized on a gas diffusion layer for the CO_2 reduction is reported by Oh *et al*. [149]. They modified the wettability of the Au/C catalyst layer by introducing a fluorine-terminated silane to the carbon black, resulting in a superhydrophobic electrode.

A hierarchical nanoporous catalyst with ellipsoidal structure for efficient CO generation from CO_2 has been carried out by Guo *et al.* [150]. The prepared nanoporous catalyst obtained a current density of 200 mA cm^{-2} at -0.30 V *vs*. reversible hydrogen electrode (RHE) with a nearly unity Faradaic effici-

ency for CO (FECO) of 98.7% under ambient conditions. Furthermore, the catalyst demonstrated continuous CO production at 100 mA cm^{-2} for 8 h at -0.6 V *vs*. RHE, maintaining a FECO greater than 98%. Recently, Monteiro *et al.* [151] investigated the feasibility of CO_2 electrolysis in acidic media (pH 2-4) using gold diffusion electrodes. The findings of this study demonstrated that achieving a high level of selectivity for CO is also feasible under these acidic conditions. The gold gas-diffusion electrode exhibited Faradaic efficiencies between 80-90% for CO at current densities up to 200 mA cm^{-2}. Apart from the aforementioned researchers, recently many reviewers had discussed about design, synthesis, developing and challenges on nanocatalyst for CO₂RR [151-155].

In 2019, Chae *et al.* [156] utilized electrospray pyrolysis to deposit silver nanoparticles onto carbon paper, creating a GDE. This GDE, featuring active silver nanoparticles, was suitable for use in continuous flow cells or similar setups. It demonstrated excellent performance for CO_2 reduction, even at high current density conditions. Likewise, Cheng *et al.* [157] introduced a solar-driven device for the highly efficient reduction of CO_2 to generate CO. Their approach involved a flowby reverse assembled GDE cell, where silver nanoparticles were directly integrated with a triple junction solar cell. This unique configuration facilitated the effective conversion of solar energy into chemical energy with high efficiency. An exceptional performance of copper selenide nanocatalysts for the electrochemical reduction of carbon dioxide to methanol is reported by Yang [158]. They achieved a high current density of 41.5 mA cm^{-2} with a Faradaic efficiency of 77.6% at a low overpotential of 285 mV.

(v) Electrolyte: The nature of the electrolytes has been known to affect almost every electrochemical process and it needs to be carefully prepared for more active and selective ERC process [54,159,160]. In fact, the same metal electrode but with a different type of electrolytes revealed different current density, product selectivity and energy efficiency in ERC process [20,161-163]. Water is commonly used as a solvent and supporting electrolyte in the ERC process. Its presence enhances the mobility of ions participating in electrochemical reactions by improving the conductance of ions within the medium [164].

The composition of the electrolyte plays a crucial role in the ERC process as it can influence several key factors. Firstly, it affects the solubility of CO_2 in the electrolyte, which is important for the availability of CO_2 molecules at the electrode surface [165]. The concentration of CO_2 in the electrolyte can impact the reaction kinetics and the overall efficiency of CO_2 reduction. Additionally, the electrolyte composition can affect the particular adsorption of reactants, particularly CO_2 and other intermediate species, onto the electrode surface [165,166]. The specific adsorption refers to the bonding of species to the electrode surface, which can impact both the rate of the reaction and the selectivity of the process.

The reduction mechanism and reaction pathways in the ERC process can also be influenced by the electrolyte composition. Different electrolytes can promote different reaction pathways and lead to the formation of different products. The existence of specific ions or additives in the electrolyte can

catalyze certain reactions or favour the formation of particular products [167]. Ultimately, the composition of the electrolyte can have an impact on the distribution of products in the ERC process [168]. Different electrolytes can result in varying selectivity towards specific products, such as CO, formate, ethanol or methane. The choice of electrolyte composition is therefore important in tailoring the desired product distribution in CO_2 reduction. Overall, the composition of electrolyte in the ERC process has a significant impact on various aspects, including solubility of CO_2, specific adsorption, reduction mechanism, reaction pathways and product distribution. Optimization of the electrolyte composition is essential for achieving efficient and selective CO_2 conversion [16,20,51,58,169].

One vital attribute of the electrolyte that affects the ERC process is pH of the electrolyte. The pH of the electrolyte control the proton availability for the reaction Further, depend on electrolyte pH, the CO_2 that is in a dissolved state in the electrolyte exists in various forms [170,171] *e.g.*, CO_2 gas ($CO_{2(g)}$); liquid (solvated) CO_2 ($CO_{2\,(liq)}$); carbonic acid (H_2CO_3); bicarbonate ion (HCO_3^-); and carbonate ion (CO_3^{2-}). As it is complicated to make a distinction between $CO_{2\,(liq)}$ and H_2CO_3, both $CO_{2\,(liq)}$ and H_2CO_3 generally take into account as one component. The dissolution of $CO_2(g)$ in to CO_2 (l) and in turn carbonic acid as governed by Henry's law. According to Henry's law, the correlation between the CO_2 concentration in the liquid phase and its corresponding concentration in the gas phase that interfaces with the liquid [172]. In the case of CO_2 reduction, this principle is relevant for understanding the solubility of CO_2 in the electrolyte.

When CO_2 dissolves in water, it forms carbonic acid (H_2CO_3), which is a weak Lewis acid. Carbonic acid readily dissociates to form bicarbonate ions (HCO_3^-) in the presence of water. If the electrolyte contains any cations, the bicarbonate ions can react with them to form insoluble carbonate ions (CO_3^{2-}). This can lead to the precipitation of carbonates and affect the availability of CO_2 for the electrochemical reactions. Furthermore, when CO_2 is purged through alkaline solutions, it can form bicarbonate and carbonate species. These reactions further limit the stability and suitability of electrolytes for CO_2 reduction, particularly in alkaline conditions.

As a result, electrolytes utilized for CO_2 reduction generally fall within the range of neutral to acidic pH [165]. Operating in these pH ranges helps to prevent the formation of insoluble carbonates and maintain the solubility of CO_2 in the electrolyte. Neutral and acidic electrolytes provide a suitable environment for CO_2 reduction reactions and enable control over the reaction pathways and product selectivity [173]. It is important to observe that the choice of electrolyte pH is just one aspect to consider when optimizing CO_2 reduction reactions [174]. Several factors, including the selection of catalyst, electrode materials and reaction conditions, are vital in attaining efficient and selective conversion of CO_2.

Several authors studied and reported the distribution of this CO_2 speciation *vs*. solution pH relationship [15,170]. Above pH 10 the solution mainly contains CO_3^- whereas below 4 the solution contains H_2CO_3/CO_2. The ERC experiments have to be carried out in an electrolyte having a pH value less than

six because of difficulty in reducing previously negatively charged HCO_3^- and CO_3^{2-} ions. But at low pH electrolytes, CO_2 reduction reactions struggle with HER. Therefore, to enhance the CO_2 reduction reaction over HER an appropriate CO_2 reduction catalyst should be employed [170,171,175].

Various researchers [34,162,163,176-179] studied the function of the cations and anions in the electrolyte. Murata & Hori [163] investigated the impact of alkali cation species on the electrochemical process. They observed a decreasing impact of the hydrogen evolution reaction (HER) in the subsequent order: lithium (Li^+) > sodium (Na^+) > cesium (Cs^+) > potassium (K^+). On the other hand, the production of hydrocarbons and alcohols was found to be highest with sodium and potassium ions. This difference in product distribution was attributed to the particular adsorption of the cations on CO_2 and its intermediates. Additionally, the choice of cation influenced the local pH at the electrode, as different cations provided different buffer capacities, which in turn affected the nature and quantity of the products formed. The researchers concluded that among the alkali cations studied, Cs^+ stood out due to its larger size and softer nature, as well as its low hydration number, enabling easy adsorption on the electrode with the lowest potential.

Schizodimou *et al.* [34] also recently reported the utilization of supporting electrolytes containing multivalent cations can impact the efficiency of ERC. Thorson *et al.* [177] highlighted the importance of cation size and its influence on th electrochemical processes. They observed that the occurance of larger cations like Cs^+ and Rb^+ in the electrolyte resulted in an increased partial current density for CO formation, surpassing the production of H_2. Similarly, Setterfield-Price & Dryfe [178] investigated the influence of tetrabutylammonium (TBA) cation and found that it exhibited significantly higher current efficiency for CO_2 reduction compared to other commonly used cations. Furthermore, no evidence of deactivation with the TBA cation has been observed, thus indicating its potential as an effective and stable catalyst for CO_2 reduction.

Furthermore, Hori *et al.* [162] also emphasized the significance of the choice of anions and their buffer capacities in the ERC process. It was observed that different anions, such as those present in $KHCO_3$, KCl, $KClO_4$ and K_2SO_4, favoured the formation of hydrocarbons. On the other hand, the presence of K_2HPO_4 promoted the hydrogen evolution reaction. This phenomenon is attributed due to the neutralization of hydroxide ions (OH^-) by HPO_4 ions at the electrode surface, which facilitated the preferential evolution of hydrogen. A similar study was conducted by Wu *et al.* [75] and highlighted performance and selectivity of Sn electrodes for production of $HCOO^-$ depends on the type of electrolyte used. Their results showed the anion SO_4^{2-} favours higher Faraday efficiency and energy efficiency whereas high production rate of $HCOO^-$ was enabled by HCO_3^-.

Based on the findings of the investigations, it can be hypothesized:

(i) The adsorption behaviour of the cation on the electrode surface is significantly influenced by its properties. This modification in adsorption behaviour alters the potential of the outer layer Helmholtz plane (OHP) within the electrical double layer (EDL), thus influencing the energetics and kinetics of the reactions present at the electrode interface.

(ii) The properties of the anion have an impact on the buffer capacity and local pH at the electrode. As a result, the availability of protons, which directly affects the reaction kinetics, is regulated. The buffer capacity and local pH play a critical role in determining the reaction rates and pathways within the electrochemical system.

Various electrolytes have been tried by researchers as an attempt to find the suitable electrolyte that possesses all ideal characteristics as an electrolyte for ERC. Based on the reviewed literature the electrolytes can be classified into three groups:

(i) Aqueous electrolytes: The majority of the early-stage studies in ERC have been used aqueous solutions as electrolytes and till now some researchers using aqueous solutions as an electrolyte, since it is easy to prepare and for using in existing electrochemical cell designs. Gattrell *et al.* [20] reviewed the ERC to hydrocarbons at copper electrodes in aqueous solutions. Hori [27,162,176,180,181] extensively used aqueous solutions to perform his early-stage ERC experiments. A 0.2 M Na_2SO_4 aqueous solution used by Summers *et al.* [28] to study the ERC of aqueous CO_2 to methanol at Mo electrode with low overpotentials. Azuma *et al.* [47] to study the ERC on various metal electrodes used aqueous $KHCO_3$ solution. Cook *et al.* [182] conducted research using a $KHCO_3$ solution to study the ERC on glassy carbon electrodes with *in situ* electrodeposited copper. A 0.5 M NaOH aqueous solution used by Innocent *et al.* [183] to study the ERC in filter press cell and they reported 65-90% Faraday efficiency of formate. In 2012, Chen *et al.* [80] used aqueous $NaHCO_3$ solution to investigate the significance of tin oxide nanoparticles in improving the efficacy of ERC on Sn by evaluating the performance of Sn electrodes treated by different pre-electrolysis treatments. The nanostructured tin catalysts for selective ERC to formate, Zhang *et al.* [129] used 0.5 M aqueous $NaHCO_3$ solution. The size dependant CO_2 reduction activity over 2.4-10.3 nm size palladium nanoparticles has been reported by Gao *et al.* [134] by performing ERC experiment in H-type cell by using 0.1 M $KHCO_3$ solution. In 2019, Tomisaki *et al.* [184] investigated the switchable product selectivity by using $KClO_4$ aqueous solution and KCl aqueous solution as electrolytes using boron-doped diamond electrodes in the ERC process.

Despite these extensive applications of aqueous solution in ERC, there are number of negative aspects such as: (i) Low solubility of CO_2 in water (0.034 M) leads to dilute concentrations even in a saturated aqueous electrolyte; (ii) high mass transfer resistance due to high diffusion coefficient of CO_2 in the aqueous electrolyte; (iii) selectivity for CO_2 reduction is generally limited in aqueous electrolytes due to the competing hydrogen evolution reaction (HER); (iv) increase surface contamination due to impurities present in the electrolyte; (v) increase in overpotential due to slow reaction kinetics; and (vi) increased difficulty in separation of products as many different by products formed.

(ii) Non-aqueous electrolytes: In order to address the potential drawbacks associated with aqueous electrolyte solu-

tions in ERC experiments, researchers have made endeavors to utilize non-aqueous electrolyte solutions. These solutions offer improved solubility of CO_2 and low level of proton concentrations, thus mitigating the aforementioned concerns. In 1981, Amatore & Saveant [185] reported the mechanism and kinetic characteristics of the ERC in media of low proton availability. Kaneco *et al.* [51] by using KOH and RbOH supporting salts, studied ERC in methanol with Cu electrode. Based on their findings, the high efficiency electrochemical CO_2 conversion to ethylene method has been accomplished. The same authors also studied the ERC at an exceedingly low level of temperature (-30 °C) with a copper wire electrode in tetraethylammonium perchlorate methanol electrolyte. At −30 °C, hydrogen formation efficiency was suppressed to less than 10.1% [50].

Recently, ionic liquids have attracted great attention of researchers as non-aqueous electrolyte in ERC experiments as it capable of forming a Lewis-base adduct with CO_2 and exhibiting activity in the CO_2 reduction process [42,43,125, 126,183-188]. Rosen *et al.* [187] reported an electrocatalytic system that relies on an ionic liquid electrolyte to convert CO_2 to CO at overpotentials less than 0.2 volt. By complexation, the ionic liquid electrolyte system reduced the energy of the CO_2^- intermediate and in turn reduced the initial reduction barrier. At Faraday efficiency greater than 96%, the system continued for 7 h and produced CO. Further, Rosen *et al.* [42] in another work presented an alternate route, addition of 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMIM-BF₄) to suppress water electrolysis and observed the addition of EMIM-BF₄ to water actually improved the efficacy of CO_2 conversion to CO. In 2015, Medina *et al.* [43] proved that without the need for an expensive supporting electrolyte bismuth–CO evolving catalyst platform can selectively catalyze the conversion of CO_2 to CO in the existence of appropriate imidazolium based ionic liquid promoters. Nevertheless, the constraints in using ionic liquid since it is expensive and need excellent information about different type of ionic liquid to decide appropriate ionic liquid for ERC. In 2019, Shironita *et al.* [189] conducted a study on the direct ERC using a three-phase interline gaseous CO_2/liquid molten salt/solid electrode system, referred to as GLS-3PI. This approach offers an isolation strategy for engineering molten salt electrolysis cells specifically for CO_2 reduction purposes.

(iii) Solid polymer electrolytes: To resolve the limitations faced by aqueous and non-aqueous systems solid polymer electrolytes (SPE) are being considered by several researchers [182,189-195]. In single proton exchange (SPE) systems, the CO_2 gas is directly fed into the catholyte compartment and the SPE fulfills various functions such as proton conduction, separation of product gases and electrical insulation of the electrodes. Suitable solid polymer electrolytes, such as perfluorinated sulfonic acid copolymers including Nafion®417 and Nafion® 117, can be chosen for their ability to conduct hydrogen ions. The working electrode, located on the cathode side of the membrane, is responsible for the reduction of CO_2 and can be constructed using carbon materials. In contrast, the counter electrode plays a crucial role in generating hydrogen ions, which are then transferred to the cathode side to facilitate the reduction

reaction. SPE have several advantages over other electrolytes such as: (a) The use of the gas phase in direct ERC eliminates the mass transfer resistance, allowing for efficient reaction kinetics. Furthermore, this approach overcomes the limitation of low solubility of CO_2 in liquid electrolytes; (b) by eliminating the presence of solvents in gas-phase reactions, the risk of catalyst poisoning is minimized, resulting in enhanced catalytic activity and selectivity compared to reactions conducted in solution-phase; (iii) gas-phase electrochemical reduction is advantageous in terms of handling and fabrication. The solid electrolyte used in this approach has good tensile strength, enabling the production of thin films with low resistance; (iv) the gas-phase system exhibits reduced electrode erosion and leakage, resulting in improved durability and stability of the electrochemical cell; and (v) gas-phase reactions facilitate easy separation of the reaction products, simplifying downstream processes for product recovery and purification

In 1995, Nishimura *et al.* [196] used selemion as SPE and Au as cathode catalyst and produced only CO as a product. In 2006, Subramanian *et al.* [197] conducted a study on the ERC to formate using a Pb electrode in an electrochemical membrane reactor and achieved a high maximum current efficiency of 93%. The study utilized two different types of membranes, namely Nafion® 961 and Nafion® 430, as solid electrolytes. Similarly, Delacourt *et al.* [140] employed a modified SPE, which incorporated a pH buffer layer between the silver-based cathode and the Nafion membrane. This modification significantly enhanced the selectivity of cathode towards the reduction of CO_2 to CO. However, a challenge that arose during long-term electrolysis was the observed alteration in product selectivity. In 2011, Narayan *et al.* [141] adopted an alkaline ion-exchange membrane in a polymer electrolyte membrane cell and the Faraday efficiency of formate reached a constant value of 45–50%. In 2012, Aeshala *et al.* [193], studied ERC in a reactor by adopting both anionic and cationic SPE cast Nafion membrane and SPEEK were developed. Their results were encourage especially promoting the composite anionic membrane (Amberlyst/SPEEK) because as desired the composite membrane worked in the low alkaline region. Regardless of these important research findings to effectively use SPEs for the ERC, further research is still required.

Effect of operating conditions: Although the operating conditions such as pressure and temperature can significantly affect the overall effectiveness of the ERC process yet it did not explore as electrodes and electrolytes. Only a few studies focused on the effect of operating conditions. The subsequent sections provide an analysis of the impact of each of these parameters in isolation.

Pressure: The limited solubility of CO_2 in the reaction medium is a major constraint in adopting any CO_2 conversion technique. The CO_2 dissolution process into reaction medium is ruled by Henry's law. As per Henry's law, the CO_2 concentration in the liquid phase (*i.e.* reaction medium) is directly proportional to the partial pressure of CO_2 in the gas phase (*i.e.* feed gas) that is in contact with the liquid phase (eqn. 3).

$$\rho_{CO_2} = K \times X_{CO_2} \qquad (3)$$

where ρ_{CO_2} is the partial pressure of CO_2 in the gas phase (Pa); K is solubility constant; and X_{CO_2} is the equilibrium mole fraction of CO_2 solute in the liquid phase. The solubility constant K is a pressure and temperature depended on parameter of the liquid phase [198]. To speed up the CO_2 solubility and in turn the reaction process, generally pressurized gas phase is applied.

In 1994, Hara *et al.* [199] conducted a study on high-pressure ERC using a copper electrode. They observed that the selectivity of the electrochemical reduction products on the copper electrode in an aqueous solution was significantly influenced by the pressure. The researchers noted that increasing the CO_2 pressure resulted in an increased flux of CO_2 to the copper electrode surface. Furthermore, they also found that the main reduction product changed in the following order: H_2 < hydrocarbons < CO < HCOOH, indicating a shift in product selectivity with rising CO_2 pressure.

The same authors in 1995, reported the effect of pressure on a range of electrodes in an aqueous electrolyte [48]. At 1 atm, the foremost products on Zn, Au, Ag, Pb and In electrodes were CO or formic acid. By increasing the CO_2 partial pressure, the total current density on the cathodic voltammograms was increased. Regarding elements belonging to the 8th to 10th group of the periodic table, such as Ni, Co, Rh, Fe, Pt and Pd at 1 atm primarily hydrogen was formed by reduction of water. However, under high pressure, the key reduction products were CO and/or formic acid. In both instances, with pressure, the total current density only slightly changed. The same group conducted a study on ERC using a glassy carbon electrode in 1997, observing the beneficial effects of increased pressure. They reported these findings, highlighting the positive impact of elevated pressure [200]. Additionally, Furuya *et al.* [201] and Sonoyama *et al.* [202] suggested the advantageous influence of pressure in relation to the usage of gas diffusion electrode. In 2002, Aydin *et al.* [203] conducted a study on ERC at low overpotential values (-0.40 V *vs*. SCE) using polyaniline (PAn) electrodes under high pressure conditions. They observed that as the pressure was increased, the current density in the system also increased gradually. It was found that the maximum Faradaic efficiency for the formation of different products varied with pressure. The maximum Faradaic efficiency values reported were 13.1% for formic acid formation, 26.5% for formaldehyde formation and 57% for acetic acid formation. These results indicate that the selectivity of the electrochemical reduction products on polyaniline electrodes under high pressure conditions can be influenced by the specific reaction conditions.

Temperature: The solubility factor K in eqn. 3 exhibits a strong dependency on temperature. Typically, as the temperature within the reaction medium rises, the dissolution of CO_2 tends to decrease. Several researchers reported the effect of temperature on product distribution in ERC process and attempts were made by researchers to adopt temperature less than room temperature to obtain optimum efficiency in ERC experiments [28,34,47,53,186,204-206]. In 1985, Ogura & Fujita [35] reported the important effect of temperature on ERC using Ruteflon electrode and the Faradaic efficiency was as high as 42% at 60 ℃. Further in 1986, the same research group studied the temperature effect by using Mo based electrode [28]. Prof.

Hori's group in 1986 [204] studied the ERC with galvanostatic electrolysis between 0 and 40 ℃ at copper electrode. At 0 ℃, the Faradaic efficiency of CH_4 formation was about 65% and it had been dropped with temperature. While the Faradaic efficiency of C_2H_4 formation had been increased with temperature and Faradaic efficiency of C_2H_4 formation at 40 ℃ was 20% [204]. A comparable results were also reported by Kaneco *et al.* [205] across the temperature range spanning from -2 ℃ to 15 ℃. Kim and coworkers [53] reported by decreasing the temperature the hydrogen formation was considerably depressed. They also found the reaction rate was increased at 0 ℃ in comparison with 22 ℃ from 0.3 mmol m^{-2} s^{-1} to 0.2×10^{-4} mol m^{-2} s^{-1}. The research conducted on the ERC using ionic liquids suggest that these liquids possess advantageous properties that enable efficient CO_2 reduction at lower temperatures [42,184]. The results recommend that low temperatures increase CO_2 solubility and manipulate optimistically the adsorption equilibrium.

Conclusions

There are several options for carbon dioxide capturing and storage (CCS) and carbon dioxide capture and utilization (CCU) to capture CO_2 emissions from specific sources such as coal power plants and industrial processes involving coal burning. The primary objective is to hinder the emission of CO_2 into the atmosphere. The main distinction between CCS and CCU lies in the ultimate fate of the captured CO_2. In CCS, the captured CO_2 is transported to an appropriate location for pro-longed storage, whereas in CCU, the captured CO_2 is transformed into commercially viable product. As long-term storage of CO_2 does not have encouraging perspective at present the scientific community mostly interested in developing various CCU technologies rather than CCS. Among the different available and tested CCU options, the converting of CO_2 into value-added chemicals has emerged as a highly crucial solution to address the escalating CO_2 emission crisis. Among the existing technologies for transforming CO_2 into other valuable chemicals, the electrochemical reduction of CO_2 (ERC) offers simultaneous solutions to two pressing contemporary challenges. These challenges encompass the global warming associated with CO_2 and the storage of renewable energy. This review paper provides a preface to the ERC process and an inclusive review of several decades of research work on ERC process by analyzing the adopted various and novel cathode materials, electrolytes and cell configuration. Further, the effect of operating conditions also discussed.

One of the main challenges in ERC process is the selection of suitable catalyst as cathode material, which provides excellent Faradaic efficiency, energy efficiency, low overpotential and high-quality product selectivity along with long-term stability. Beyond several new transition metals such molybdenum, rhodium, ruthenium, *etc.* alloying of different metals also have been studied by researchers as alloying optimize the binding energy of reaction intermediates. Another main issue in ERC process is related to hydrogen evolution reaction (HER). To overcome this issue high overpotentials have been used which reduce the energy efficiency of the process. To avoid this issue non-aqueous electrolytes have been tried by researchers and

this strategy suppresses the hydrogen formation. Several researchers considered the use of solid polymer electrolytes (SPE) as a potential solution to address the restrictions encountered in both aqueous and non-aqueous systems. In these systems, the direct feeding of CO_2 occurs through the catholyte compartment and the solid polymer electrolyte (SPE) plays multiple roles, including proton conduction, product separation and electrical insulation of the electrodes. Despite significant research findings, further investigation is necessary to successfully utilize SPEs for the ERC.

Continuous improvements have been made to the cell configuration in order to enhance mass transfer effects and improve the separation of reaction products. The inclusion of gas diffusion electrodes (GDEs) has introduced a novel trend in ERC by creating a three-phase interface among the gaseous reactants, solid catalyst and electrolyte. However, no electrochemical cell system has yet been proven to be flawless in terms of electrodes, electrolytes and cell configurations. Extensive future research is therefore required to fully replace existing CO_2 mitigation technologies with the ERC process.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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