Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Green Chem. RSCPublishing

ARTICLE

Towards the electrochemical conversion of carbon dioxide into methanol

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Various strategies have been proposed to date in order to mitigate the concentration of CO_2 in the atmosphere, such as the separation, storage, and utilization of this gas. Among the available technologies, the electrochemical valorisation of CO_2 appears as an innovative technology, in which electrical energy is supplied to establish a potential between two electrodes, allowing CO_2 to be transformed into value-added chemicals at mild conditions. It provides a method to recycle CO_2 (in a carbon neutral cycle) and, at the same time, a way to chemically store the excess of renewable energy from intermittent sources reducing our dependence on fossil fuels. Among the useful products that can be obtained, methanol is particularly interesting as platform chemical, and it has gained a renewed and growing attention in the research community. Accomplishments to date in the electroreduction of CO_2 to methanol have been encouraging, although substantial advances are still needed to become a profitable technology able to shift the society to renewable energy sources.

This review presents a unified discussion of the significant work that has been published in the field of electrocatalytic reduction of CO_2 to methanol. The work emphasizes on aspects related with process design at different levels: cathode materials, reaction media, designs of electrochemical cells, as well as working conditions. It will then extend the discussion to the important conclusions from different electrocatalytic routes, and recommendations for future directions to develop a catalytic system that will convert CO_2 to methanol at high process efficiencies.

1. Introduction

In the last century with the intensification of human industrial activities, the balance between the CO_2 produced and consumed on earth has gradually been disrupted, leading to more CO_2 emissions and making global warming a pressing issue. Therefore, reducing CO_2 production and converting this molecule into useful materials seems to be necessary, indeed critical, for environmental protection, and various governments worldwide have signaled their concern by increasing their investment in research to address this issue. There are different approaches to tackle the CO_2 issue which include to capture CO_2 and either store it,[1-3] or to convert the CO_2 into valuable chemicals.[4-6] The recycling of CO_2 molecule by electrochemical reduction (also known as artificial photosynthesis), where electrical energy is supplied to establish a potential between two electrodes in order to allow CO_2 to be transformed into reduced forms, has attracted worldwide interests due to its potential environmental and economic benefits.[4,7-10] This technology, coupled to a renewable energy source, such as wind or solar, could generate carbon neutral fuels or industrial chemicals that are conventionally derived from petroleum. The reduction of global CO_2 emissions and the conversion of this wasted CO_2 into industrially useful chemical feedstocks clearly align this process with the principles of sustainable chemistry (or green chemistry), as observed in recent review publications in this journal.[11-13]

Moreover, the imbalance between the energy production and consumption is particularly important for the renewable energy sources, whose outputs depend on natural factors. In this scenario, CO_2 electroreduction could solve, or help to solve, this imbalance, utilizing surplus energy into methanol production. The development of a cost effective process for the electrochemical reduction of CO_2 could enable a shift to a sustainable energy economy and chemical industry.

The electrochemical reduction of CO_2 was studied for the first time in 1870 by Royer.[14] Since then, it has been the subject of a large number of publications, especially during the last twenty years. These works have been summarized in several specific review articles on CO_2 electrochemical reduction where the state of the art is presented with different perspectives,[4, 15-32] as listed in Supplementary information (Appendix I).

Nowadays, CO_2 capture, conversion, and utilization is still recognized as a feasible and promising cutting-edge area of exploration in energy and environmental research, but a deep understating, not only of the CO_2 reduction mechanisms, but also of economic viability and life cycle assessment, is still required, although some efforts have already been done.[8,33-35]

Recently, Dominguez-Ramos et al. evaluated the environmental sustainability of the CO_2 electroreduction process, focusing on resources and greenhouse gas emissions. They concluded that the integration of renewable energy and the reduction in the consumption of chemicals in the electrolysis, might lead this technology to be a potential candidate for an environmentally sustainable CO_2 utilization.[34]

The direct electrochemical reduction of CO_2 results in a variety of products, which depend mainly on catalyst materials and the reaction medium. Electrochemical reduction of CO_2 can mainly proceed through two, four, six, and eight-electron reduction pathways in gaseous, aqueous, and non-aqueous phases at different cell and electrode configurations. The major reduction products are carbon monoxide (CO), formic acid (HCOOH) or formate ($HCOO^-$) in basic solution, formaldehyde (CH_2O), methanol (CH_3OH), oxalic acid ($H_2C_2O_4$) or oxalate ($C_2O_4^{2-}$) in basic solution, methane (CH_4), ethylene (CH_2CH_2) or ethanol (CH_3CH_2OH).[32] Among the various chemicals, the challenges for converting CO_2 into CH_3OH are great, but the potential rewards are also enormous.

1.1. Potentialities for the electrochemical reduction of CO_2 to CH_3OH

Methanol is a green fuel with almost half of the energy density of the mostly used fuel, gasoline (methanol: 15.6 $MJ\cdot L^{-1}$; gasoline: 34.2 $MJ\cdot L^{-1}$),[36] but also a vital intermediate for several bulk chemicals used in day-to-day life products such as silicone, paint, and plastics. Compared to hydrogen, CH_3OH possesses a higher energy density, it can be stored at atmospheric pressure, and it can be utilized directly in energy converting systems like internal combustion engines, due to its high octane rating, or directly in fuel cells in Direct Methanol Fuel Cells (DMFC) or indirectly (after conversion into hydrogen by reforming).

At present, most of the commercial CH_3OH is produced from methane through syngas (the mixture of CO and H_2) by steam reforming on quite large-scale industrial plants in several million tons per year capacity.[10] However, the electrochemical transformation of CO_2 emitted from fossil fuel burning power plants and other industries (and eventually even the CO_2 contained in the air) into CH_3OH can be performed under ambient conditions. This process could become feasible and renewable at human timescale, contributing to solve both global warming and energy crisis problems to a great extent.[10,37]

The “methanol economy”, in which CH_3OH replaces fossil fuels as a form of energy vector, transportation fuel and raw material for synthetic hydrocarbons and their products, was firstly proposed by the Nobel Laureate Olah and widely discussed afterwards by his collaborators.[10,38,39] In these publications, they summarized the state of our current energy sources, their availability and limitations before suggesting a new approach in the so-called methanol economy. In this economy, energy can be stored in the form of CH_3OH and the CO_2 is recycled avoiding additional emissions, as represented in Figure 1.

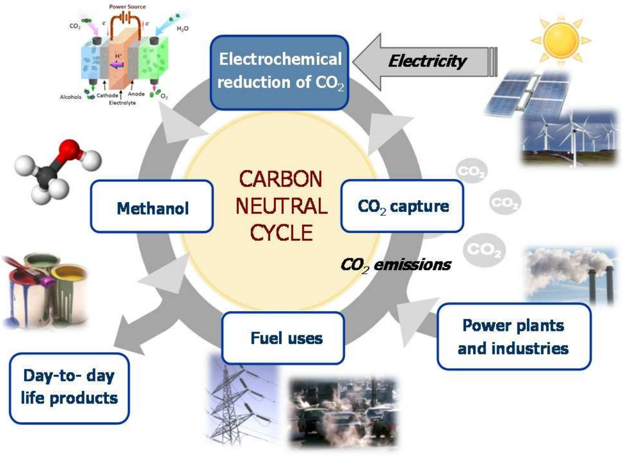

Figure 1. The methanol-based economy cycle model.

A close study of the existing information on this subject reveals that the successful development of an artificial photosynthesis is no longer an unrealistic dream. The literature reported so far the conversion of CO_2 into CH_3OH following thermochemical, electrochemical, photoelectrochemical, and photocatalytic reactions performed over both inorganic as well as organic molecular (homogeneous and heterogeneous) catalytic systems.[32] Nevertheless, none of the review articles exclusively deals with the literature on the electrochemical conversion of CO_2 into CH_3OH, taking into consideration the effect of the applied catalytic material, electrolyte and configuration of the electrochemical cell.

To fill this gap, this review article presents and discusses the several fundamental aspects and opportunities of CO_2 electroreduction to CH_3OH, with a main perspective of designing a simple, efficient and reliable method for the continuous electroreduction of CO_2 using renewable energy resources. The following key points of the CO_2 electroreduction process to CH_3OH are discussed: (i) cathode materials applied, (ii) effect of the reaction medium, (iii) operating conditions, (iv) configuration of the electrochemical cell and, finally (v) a comparison with other electrocatalytic routes. Besides, this review also discusses some other relevant CO_2 electrocatalytic approaches, which despite the fact that their main objective is not CH_3OH production but other products, whose results may be taken into account for the development of an efficient process to generate CH_3OH and identify research needs.

2. Summary of studies

The overall reaction of CH_3OH formation is a combination of a reduction and oxidation reaction at the cathode and anode of the system, respectively, as presented in Table 1.

Table 1. Electrochemical reaction for CO_2 conversion to CH_3OH under standard conditions.

	Electrochemical reaction	*E* (V)
Cathode	$CO_2 + 6H^+ + 6e^- \leftrightarrows CH_3OH + H_2O$	-0.22 vs. SCE
Anode	$3H_2O \leftrightarrows 1.5O_2 + 6H^+ + 6e^-$	0.99 vs. SCE
Overall:	$\mathbf{CO_2 + 2H_2O \leftrightarrows CH_3OH + 1.5O_2}$	**1.21**

Thermodynamically, it is feasible to electrochemically reduce CO_2 to CH_3OH; however, the reduction potential of carbon dioxide is only 20 mV positive with respect to the potential for water reduction, which results in hydrogen generation. Then, in the electrochemical reduction of CO_2 to CH_3OH, the electrical energy supplied to the system is consumed by two reactions:

(i) Hydrogen Evolution Reaction (HER), in which the energy is consumed for the production of hydrogen through the process of water electrolysis.

(ii) The reduction of CO_2 into the product of interest, CH_3OH.

In order to achieve high selectivities for a given product (defined by the Faradaic efficiency) and high production rates of the desired CH_3OH, it is required to use an electrode material able to suppress the HER so that most of the electric energy supplied is consumed only in the CO_2 reduction reaction.

Figure 2 shows the two most probable reaction pathways in the formation of CH_3OH from the electrochemical conversion of CO_2.[40] The first mechanism proceeds through CO pathway,[19,41] and the second undergoes formate ($HCOO^-$) intermediate.[42-44] The other main compounds that are expected to be formed together with CH_3OH are CO, HCOOH, CH_2O and CH_4. For example, in 2012, Kuhl et al.[45] evaluated the electrochemical reduction of CO_2 on metallic copper surfaces across a range of potentials and observed a total of 16 different CO_2 reduction products (CH_3OH, CO, CH_4, acetate, acetaldehyde, ethanol, ethylene, allyl alcohol, propionaldehyde, 1-propanol, glyoxal, glycoaldehyde, ethylene glycol, hydroxyacetone, acetone). Since the transformation of CO_2 to CH_3OH requires $6e^-$ the reduction reaction is considered to be kinetically slower; hence, very active and selective catalytic materials for this reaction are needed.

(a)

$$CO_2 + e^- + H^+ \text{ (at cathode surface)} = HOCO^- \text{ (dioxymethylene ion)}$$
$$HOCO^- + e^- + H^+ = H_2O + \underline{CO} \text{ (carbon monoxide)}$$
$$CO + e^- + H^+ = HCO$$
$$HCO + e^- + H^+ = \underline{CH_2O} \text{ (formaldehyde)}$$
$$HCHO + 2e^- + 2H^+ = CH_3OH$$

$$\text{Overall: } CO_2 + 6H^+ + 6e^- = CH_3OH + H_2O$$

(b)

$$CO_2 + e^- + H^+ = HCOO^- \text{ (formate ion)}$$
$$HCOO^- + e^- + H^+ = \underline{HCOOH} \text{ (formic acid)}$$
$$HCOOH + e^- + H^+ = HCO + H_2O$$
$$HCO + e^- + H^+ = \underline{CH_2O} \text{ (formaldehyde)}$$
$$HCHO + 2e^- + 2H^+ = CH_3OH$$

$$\text{Overall: } CO_2 + 6H^+ + 6e^- = CH_3OH + H_2O$$

Figure 2. Probable reaction pathways in the electrochemical reduction of CO_2 to CH_3OH, through CO (a) and HCOOH (b) intermediates.

2.1. Applied cathode materials

Transition metals and their associated compounds, such as metal complexes, have been widely evaluated for the electroreduction of CO_2. This is probably because these metals have vacant orbitals and active *d* electrons, which are believed to be able to energetically facilitate the bonding between the metal and the CO_2 for adduct formation and facilitate the desorption of the reduction products.[32] Besides, the electronic and geometric properties of the metallic catalysis surface, in relation to the size of the active centres and the elements forming them, seem to be crucial to block HER and promote CO_2 reduction.[46]

Among the available metals, those identified in Figure 3 have been reported to be the most active for the electrochemical transformation of CO_2 to CH_3OH and their use is discussed in the following sections. The metals have been grouped according to their use for preparing cathode materials (as reported in literature), as well as to their position in the periodic table of elements.

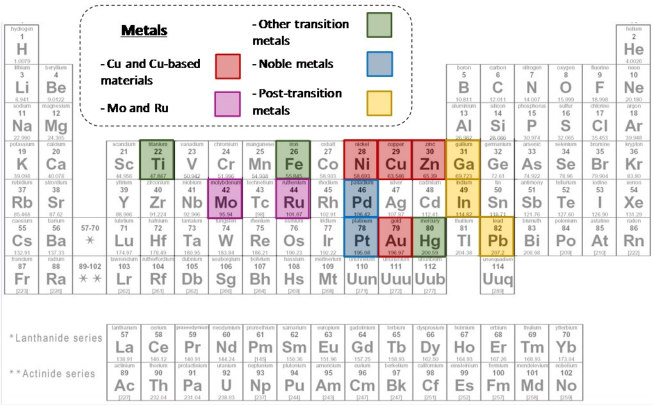

Figure 3. Active metals reported in literature for the electrochemical transformation of CO_2 into CH_3OH.

2.1.1. Copper (Cu) and Cu-based electrodes

Among the various metal electrodes employed for the electrochemical reduction of CO_2, copper (Cu) is one of the most promising materials for obtaining hydrocarbons and alcohols. The industrial catalysts for the production of CH_3OH are commonly composed of Cu-Zn-Al mixed oxides. It was demonstrated that the combination of these compounds produces a higher catalytic activity for CH_3OH formation than the isolated metals at low pressures.[47] Therefore, Cu and Zn metals were employed initially, in 1904, as cathodes for the electrochemical reduction of CO_2.[48] In this first work, Cu, Zn, and amalgamated Zn and Cu based electrodes were tested for the electroreduction of CO_2 in aqueous $NaHCO_3$ and K_2SO_4 solutions. The results showed that the electroplated Cu with amalgamated Zn electrodes exhibited high efficiency for reducing pressurized CO_2, although the main product obtained was HCOOH. In 1985 and 1986 Hori et al.[49,50] observed high rates and efficiencies for the electrochemical reduction of CO_2 to CO and hydrocarbons, mainly CH_4 and C_2H_4, on Cu electrodes in aqueous hydrogen carbonate solution. This new finding opened up the interest to evaluate Cu metal surfaces for the electrochemical transformation of CO_2. Since then, the formation of low hydrocarbons (e.g. CH_4 or C_2H_4), alcohols (CH_3OH, CH_3CH_2OH and 1-propanol (C_3H_8O)), esters, as well as high hydrocarbons, such as paraffins and olefins (up to 6 carbon atoms), have been reported in literature at Cu, electrodeposited Cu and Cu-coated electrodes.[19,49-85] Besides, recent studies[41,45,86,87], have advanced in improving the understanding of the mechanisms for the electroreduction of CO_2 at Cu-based electrodes. The results suggest that the key enabling step in the formation of hydrocarbons from CO_2 is the protonation of adsorbed CO to form adsorbed CHO. However, since CO binds only weakly to Cu surfaces, materials that bind CO weaker will lead to large amounts of gas-phase CO production. Therefore, materials that bind CHO strongly, while binding CO with similar tenacity, offer the best hope for future catalyst materials.[41]

At present, the greatest reported current densities, *j*, and Faradaic efficiencies, *FE*, towards CH_3OH formation are associated with oxidized Cu-based electrodes with current densities of up to 33 $mA\cdot cm^{-2}$ and Faradaic efficiencies greater than 100%, where chemical and electrochemical mechanisms are involved in the transformation of the CO_2 molecule.[64]

Cu and Cu oxides. In an attempt to enhance the electrochemical reduction of CO_2, oxidized-Cu surfaces have been applied since Frese et al. reported in 1991 the CO_2 electroreduction to CH_3OH at various oxidized copper electrodes (Cu foil, Cu foil thermally oxidized in air, and air-oxidized Cu electrodeposited on anodized or air-oxidized Ti foil) at ambient temperature.[64] The highest rates, $2.8\cdot 10^{-5}$ $mol\cdot m^{-2}\cdot s^{-1}$, were found when using anodized Cu in 0.5 M $KHCO_3$ at -1.90 V vs. saturated calomel electrode (SCE). The resulting apparent Faradic efficiencies were extraordinarily high (~240%).

In 2009, Chang et al.[67] synthesized Cu_2O cubes to prepare Cu_2O-catalyzed carbon clothes. These materials were characterized electrochemically by potentiostatic measurements and cyclic voltammetries in 0.5 M NaOH electrolytes saturated with CO_2. The GC/FID analysis of the electroreduction process confirmed the CH_3OH to be the predominant product. The current responses for the potential range 0 to -1.70 V (vs. SCE) revealed the electrochemical stability and the notable catalytic ability of Cu_2O-catalyzed carbon clothes for the CO_2 reduction. The mass activity was estimated to be 0.94 $mA\cdot mg^{-1}$.

Moreover, Le et al.[69] reported CH_3OH production rates as high as $1.2\cdot 10^{-4}$ $mol\cdot m^{-2}\cdot s^{-1}$ and Faradaic efficiencies up to 38% in 0.5 M $KHCO_3$ at electrodeposited cuprous thin films electrodes. These values were higher than those obtained from the electroreduction of CO_2 either at air-oxidized or anodized Cu electrodes, suggesting that Cu(I) species play a critical role in electrode activity and selectivity to CH_3OH. The theoretical potential for CO_2 reduction to CH_3OH, at pH= 7.6 and 25 ºC, occurs 20 mV positive of the standard hydrogen electrode with Cu materials, while using oxidized Cu the CO_2 reduced at more positive potentials, therefore showing greatest yields and efficiencies. Moreover, the formation of CH_3OH was stable over Cu and Cu oxides supported on ZnO for longer reaction times. They hypothesized that the stability of this species may be a key factor for maintaining catalytic activity for CH_3OH production from CO_2 electroreduction, since ZnO stabilize oxidized Cu in the hydrogenation reaction.[44,70] The mechanism for CH_3OH synthesis from CO_2, and its intermediates, on Cu/Zn surfaces has been also studied. The calculations indicated that the Cu-Zn site is the active site to catalyze CH_3OH.[70] However, more fundamental studies regarding oxidized Cu electrodes on their formal reduction potentials relative to CO_2 are still required.

In 2012, Li et al.[71] prepared Cu_2O layers by annealing a Cu foil in air. The results showed the dependency of CO_2 reduction activity with electrode layer thickness. Besides, the prepared Cu_2O electrodes (≥ 3 μm thick) exhibited 480 larger surface roughnesses than polycrystalline Cu-based electrodes and required 0.50 V less overpotential to reduce the CO_2 molecule. The electrodes prepared were stable and showed a higher level of activity than all previously reported metal electrodes evaluated under comparable conditions (>1 $mA\cdot cm^{-2}$ at overpotentials <0.40 V), although the main reduction products were CO and HCOOH. Lan et al.[72] very recently studied the electrochemical behavior of different loadings of a Cu(core)/CuO(shell) catalyst in a standard three-electrode cell. They focused on the modelling of the electroreduction process of CO_2 to CO and HCOOH by using an in-series first-order reaction. The models reasonably described the formation of the two products and could be used to further understand the formation of CH_3OH at Cu materials. The same group reported in 2014 the performance for CO_2 electroreduction at Cu(core)/CuO(shell) catalyst in a flow reactor where CO, HCOOH and CH_3OH were the main products.[84] The Faradic efficiency for CH_3OH was 42.7%. A larger amount of CH_3OH was obtained for the Cu(core)/CuO(shell) catalyst in 1 M $KHCO_3$ (-1.77 V vs. SCE) than that obtained at a Cu foil. The suggested CO_2 reduction pathway is shown in Figure 4. They concluded that the interplay between the Cu core and CuO shell is beneficial for the production of CO, HCOOH and CH_3OH.

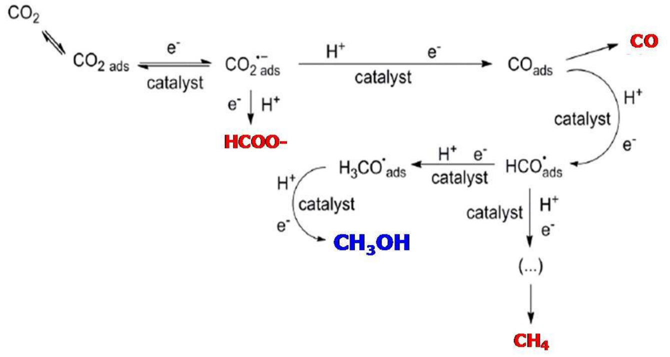

Figure 4. Possible reaction pathway for the electrochemical reduction of CO_2 to CH_3OH on Cu(core)/CuO(shell) catalyst. Reprinted from ref.[84]

Recently, de Brito et al.[88] described the photoeletrocatalytic reduction of CO_2 dissolved in 0.1 M $Na_2CO_3/NaHCO_3$ at Cu/Cu_2O electrodes prepared by electrochemical deposition of a Cu foil. The obtained values were very promising, with a CH_3OH yield as high as 80 ppm and a Faradaic efficiency of 75% under UV-Vis irradiation and bias potential of + 0.16 V vs SCE. The proposed system may inspire future works for electrochemical CO_2 conversion processes.

Cu-alloys. Alloying Cu with other metals may enhance the electrochemical properties for CO_2 reduction to CH_3OH.[63,65,73,76,77] Wanatabe et al. [69,73] reported, after studying the electrochemical reduction of CO_2 in aqueous $KHCO_3$ on 32 metal electrodes,[74,75] the peculiar effects of alloying Cu with other metals (i.e. Ni, Sn, Pb, Zn, Ag and Cd) to enhance the reversibility and selectivity for CO_2 electroreduction. The Cu-Ni electrodes prepared by electroplating yielded mainly CH_3OH and HCOOH at less negative potentials. However, the Cu-Ni-based electrodes increase hydrogen production and decrease hydrocarbon yields with the increase of Ni coverage on the surface of Cu. Besides, the current efficiency decreased with electrolysis time, which was related to the formation of poisonous intermediates.[65]

Schizodimou and Kyriacou[77] evaluated the accelerating effect of various cations and the acidity of the solution on the rate of the electrochemical reduction of CO_2 on a $Cu_{88}Sn_6Pb_6$ alloy cathode. The results showed that the rate of CO_2 reduction can be increased at low overpotentials and the distribution of the products can be controlled simply by varying the composition of the electrolyte. The main products of the reduction were CH_3OH, CO, HCOOH and CH_3CHO. The maximum current efficiency for CH_3OH formation was 36.3 % at −0.70 V (vs. SCE) with a total CO_2 reduction rate of $1.8\cdot10^{-5}$ $mol\cdot m^{-2}\cdot s^{-1}$ (44.47 $\mu mol\cdot h^{-1}$) in an acid solution (2 M HCl solution). More recently, Jia et al.[89] conducted the electroreduction of CO_2 in aqueous 0.5 M $KHCO_3$ at nanostructured Cu-Au alloys. The Faradaic efficiency of CH_3OH on $Cu_{36.9}Au_{36.1}$ supported on nanoporous Cu films (NCF) was found to be 15.9%, which was higher than in nanostructured Cu and 19 times higher than on pure Cu electrodes, as represented in Figure 5. The material catalyzed not only CO_2 reduction, but CO reduction, which contributes to enhance the conversion of CO_2 to alcohols.

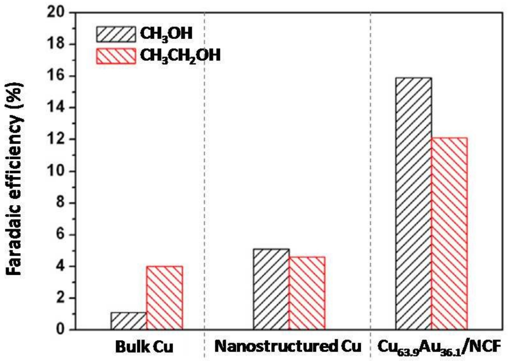

Figure 5. Faradaic efficiencies for CH_3OH and CH_3CH_2OH production by different electrodes in 0.5 M $KHCO_3$ solution. Reprinted from ref.[89], Copyright (2014), with permission from Elsevier.

Other alloys resulted in the production of HCOOH and CO with an enhanced reaction rate compared to that using the elemental metals, such as the work developed by Yamamoto et al.[76] where CO and H_2 were formed in 1:1 ratio at Cu-Ni catalysts with an overall energy efficiency of 44.6%.

Cu nanostructures and organic frameworks. In 1993 Schwartz et al.[80] firstly studied crystal structures (perovskite-type) for the electrochemical reduction of CO_2 under ambient conditions at $A_{1.8}A'_{0.2}CuO_4$ (A= La, Pr and Gd; A´= Sr and Th). The results showed Faradaic efficiencies for CO_2 reduction to CH_3OH, CH_3CH_2OH, and C_3H_8O of up to 40% at current densities of 180 $mA\cdot cm^{-2}$. In 2013, Andrews et al.[86] studied the electroreduction using Cu electrodes and Cu nanoclusters on single crystal ZnO electrodes in aqueous bicarbonate electrolytes. The products obtained at -1.45 V (vs. SCE) in gas phase included H_2, CO, CH_4 and C_2H_4, while in the liquid phase were CH_3OH, CH_3CH_2OH, $HCOO^-$, methyl formate and trace levels of C_3H_8O were detected. While the normalized current densities were similar using any type of the electrode considered at certain potential, selectivity toward CH_3OH and CH_3CH_2OH was improved by at least an order of magnitude using the nanostructured Cu/ZnO electrodes. They proposed that ZnO strengthen the $Cu\text{-}CO^-$, increasing the selectivity to alcohols. Besides, in 2014, Jia et al.[89] electrodeposited a novel nanostructured Cu-Au alloy, based on a nanoporous Cu film as a template. The linear voltammetry analysis showed that the synthesized material exhibit catalysis toward electrochemical reduction of CO_2 to CH_3OH in aqueous media. A further analysis of the products obtained (CH_3OH and CH_3CH_2OH) revealed that Faradaic efficiencies are greatly dependent on the nanostructures and compositions of Cu-Au alloys. Recently, Xie et al.[85], in an effort to overcome the electrocatalysts instability and large reaction overpotentials, prepared Cu nanoflower (NF) catalysts with chrysanthemum-like structure. The results showed a 400 mV reduction of overpotential for CH_4 and C_2H_4, in comparison to polycrystalline Cu. The electrocatalytic material keeps the catalytic activity for over 9 h and HER was reduced to 25% Faradaic efficiency. These materials offer good prospects for being used to design new electrocatalysts for CH_3OH formation.

In the past two decades, metal-organic frameworks (MOFs) have attracted research interest due to their high porosity and thermal stability, as well as adjustable chemical functionality. MOFs, or coordination polymers/networks, combine organic ligands and metal ions or metal-containing clusters. They have been widely used as effective materials for CO_2 adsorption, storage, and separation,[78] but they may also represent an opportunity in the electrochemical reduction of CO_2 emissions.[79]

Kurmar et al. studied[81] the electrocatalytic properties for CO_2 reduction of Cu-based MOFs in CO_2-saturated N,N-dimethylformamide containing tetrabutylammonium tetrafluoroborate. The cyclic voltammetric studies revealed that the electrochemically generated Cu(I) species were very selective for CO_2 reduction, although the main product was $H_2C_2O_4$. In a recent study, Hinogami et al.[82] successfully synthesized Cu rubeanate MOFs particles and dispersed them on a carbon paper to form electrodes. The resulting potential for CO_2 reduction was about 0.20 V more positive than that observed on a Cu metal electrode in an aqueous electrolyte solution. However, the major reduction product was HCOOH, whereas a Cu metal electrode could generate a range of products. In any case the production of HCOOH was 13-fold (at −1.44 V vs. SCE) than that of a Cu metal electrode and the stability was confirmed, suggesting that promising results could be also obtained for CH_3OH production with specifically designed MOFs. Maihom et al.[83] further demonstrated that MOFs can be utilized not only to capture and activate CO_2, but for CO_2 catalysis. They investigated on the reaction mechanisms of the hydrogenation of CO_2 to HCOOH over Cu-alkoxide-MOFs. The investigation of CO_2 electroreduction to CH_3OH on Cu-based MOFs electrodes, however, still remains as a challenge for future research.

2.1.2. Molybdenum (Mo) and Ruthenium (Ru)

One of the initial studies on the topic shows that Cr, Mo, W, etc. presented scarce electrocatalytic activity in the reduction of CO_2 at ambient temperatures in aqueous $KHCO_3$, in comparison to other metallic electrodes, such as In, Sn, Hg, or Cu.[58] However, in subsequent studies during mid of 1980s to mid 1990s, CO_2 was reduced over several metals and the formation of CH_3OH was observed on Mo[90-92] and several types of Ru electrodes[92-95] with Faradaic efficiencies up to 60% at current densities less than 2 $mA\cdot cm^{-2}$. Since then, these metals are well known for the electroreduction of CO_2, as well as CO_2, CO, and H_2 adsorption, leading to different catalytic activities, electrode stabilities and product selectivities.

In 1985 Frese et al.[93] firstly demonstrated the production of small amounts of CH_3OH on electroplated and Teflon-supported Ru electrodes in CO_2 saturated 0.2 M Na_2SO_4 at pH= 4-7. The Faradaic efficiency of the electroreduction process was as high as 42% at 60 ºC. One year later, Summers et al.[90] conducted the electrolysis of CO_2 using Mo electrodes in CO_2-saturated 0.2 Na_2SO_4 (pH= 4.2) and 0.05 M H_2SO_4 (pH= 1.5) solutions, producing CH_3OH as the major carbon-containing product. The reduction proceeded at room temperature and -0.57 to -0.80 V (vs. SCE) with Faradaic efficiencies near 100% in some cases. Based on these results, Frese's group patented a method for producing CH_3OH at Mo foils mounted on Cu wires, with up to 84% Faradaic efficiency and without detectable corrosion.[91] Such reductions can occur, for example, at -0.80 V (vs. SCE), only 160 mV negative of the standard potential corrected for pH. The electrolysis also produces small amounts of CO and traces of CH_4. Bandi et al.[92] used various conductive oxide mixtures (RuO_2, TiO_2, MoO_2, Co_3O_4, and Rh_2O_3) to catalyze CO_2 electroreduction to CH_3OH. The CO_2 underwent reduction to CH_3OH and HCOOH, as detected by GC, in a solution of 0.2 M Na_2SO_4 (pH= 4) saturated with CO_2. At low current densities (~50-100 $\mu A\cdot cm^{-2}$), before the onset potential of HER, there is a high current efficiency for CH_3OH formation on electrodes based on mixtures of RuO_2 + TiO_2 and RuO_2 + Co_3O_4 + SnO_2 + TiO_2 deposited on a Ti foil. The same author lately reported the electrocatalytic activity of mixed Ru/Ti materials.[94] In order to optimize the current efficiency for the reduction of CO_2 to CH_3OH, the electrodes were covered with some amounts of Cu. The results showed that when increasing the Cu deposition on the electrode surface an increase in CH_3OH production is also noted with positive effect on current efficiency. The CO_2 also underwent electrochemical reduction to CH_3OH and acetone over the surfaces of Ru, Cu–Cd-modified Ru, and Cu–Cd-modified RuOX + IrOX electrodes. The current efficiencies ranged from 15.3 to 38.2% in 0.5 M $NaHCO_3$ solution at a potential of -0.80 V (vs. SCE).[95] In 2003, Spataru et al.[96] showed that RuO_2-coated diamond electrodes could be a promising electrocatalysis material for CO_2 electroreduction. The main reduction products obtained in acidic and neutral media were CH_3OH and HCOOH, with efficiencies of 7.7 and 40 %, respectively. Moreover, when CO_2 was subjected to electrochemical reduction in 0.5 M $NaHCO_3$ solution in a two-compartment H-type electrochemical cell at Pt modified with RuO_2–TiO_2 nanotubes and RuO_2–TiO_2 nanoparticles, the formation of CH_3OH was detected.[97] Recently, Li et al.[98] prepared MoS_2-rods/TiO_2 nanotubes heterojunction electrodes for CO_2 transformation. They demonstrated that MoS_2 were hexagonal prism structures without notable effects that were randomly distributed on the TiO_2 nanotube surface, as observed in Figure 6. They concluded that the regular structure was beneficial for electron transfer, and therefore catalytic ability. Electroreduction experiments showed that the CH_3OH yield reached 202.2 $mg\cdot L^{-1}$ (6 $mmol\cdot L^{-1}$) at 6 h of experimental time with a Faradaic efficiency of 42%, which gradually decreases with reaction going on. However, when illumination was introduced, a CH_3OH yield and Faradaic efficiency of 463.68 $mg\cdot L^{-1}$ and 111.58%, respectively, can be achieved.

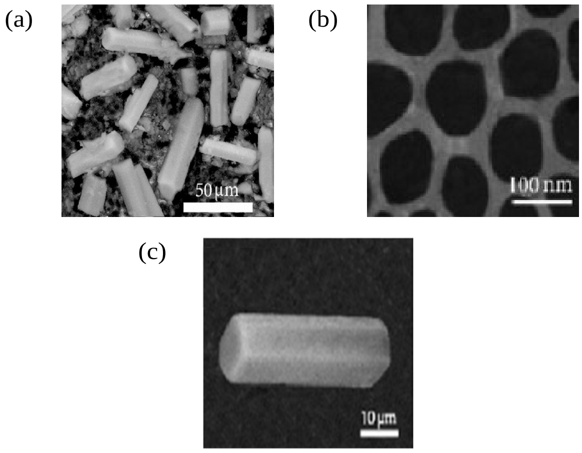

Figure 6. SEM images of (a) MoS_2-rods/TiO_2 nanotubes (at 50 μm magnification), (b) TiO_2 nanotubes (100 nm) and (c) MoS_2 rods (10 μm). Reprinted from ref.[98], Copyright (2014), with permission from Elsevier.

2.1.3. Other transition metals

Iron (Fe). In general, the electrochemical reduction of CO_2 at electrodes made of Fe, Co, and Ni or Fe/Co/Ni complexes of porphyrin, in aqueous solutions mainly gives hydrocarbons, as well as H_2 and CO. However, relatively high efficiencies for CO_2 electroreduction to CH_3OH in durable catalysts were also obtained using Fe-based complexes of porphyrin.[99]

In 1986 Ogura and Yoshida showed that CO_2 could be reduced electrochemically to CH_3OH at a ES (Everitt's Salt, $K_2Fe(II)[Fe(II)(CN)_6]$)-meditated electrode in the presence of the 1,2-dihydroxybenzene-3,5-disulfonate (tiron) ferrate(III) complex and ethanol.[100] Ogura and Fujita probed the positive performance of ES in the CO_2 electrochemical transformation to CH_3OH when they compared the Faradaic efficiency at ES-coated Pt plate electrodes (efficiency >80%)[101] with that at a quinone-derivative-coated Pt electrode (>50%).[102] These results have been further confirmed by the same group when producing CH_3OH from CO_2 in photocatalytic[103] and direct liquid fuel cells.[104] Rail and Berben[105] reported that, under appropriate conditions, $Et_4N[Fe_4N(CO)_{12}]$ could be a catalyst for CO_2 electroreduction at 1.25 V vs. SCE using a glassy carbon electrode. ES coated on a Pt plate was also found to present activity for CH_3OH formation in the presence of pentacyanoferrate(II) ($Na_3Fe(II)(CN)_5H_2O$) or amminepentacyanoferrate(II) ($Na_3Fe(II)(CN)_5NH_3$) and a alcohol (CH_3OH or CH_3CH_2OH) as an electron mediator to reduce CO_2.[106,107] The activation energies for CH_3OH formation, via HCOOH, were estimated to be 5.8-10.6 kcal·mol^{-1}, which were much higher than those determined for reduction of CO under identical experimental conditions. The proposed reduction mechanism was first the reduction of ES to PB (Prussian blue, $KFe(III)[Fe(II)(CN)_6]$) on the cathode to start the reduction by transferring electrons to CO_2.[108] Based on this observation, Ogura et al.[109] carried out a further study using a PB-polyaniline (PAn) dual film coated Pt/Co-2-hydroxy-lnitrosonaphthalene- 3,6-disulfonate complex electrode in aqueous solution. Lactic acid, ethanol, acetone, and CH_3OH were detected at a low overpotential (-0.60 V vs. SCE) under ambient conditions.[110-112] Neff in 1978 first electrodeposited PB onto a Pt plate from a mixed solution of 0.01 M $FeCl_3$ and 0.01 M$K_3Fe(CN)_6$, that was reduced to ES.[113] Other studies confirmed that CO_2 can be reduced to CH_3OH in a continuous electrochemical process if the PB formed from ES is continuously reduced back to ES by supply of electricity, with no degradation of the metal complex.[99-98,107,114-118] When a mixture of KCl, CH_3OH and metal complex was employed as an electrolyte, CH_3OH was identified as the sole reduction product. These results suggest that the simultaneous existence of a metal complex and CH_3OH is appropriate for the reduction of CO_2 into CH_3OH.[119]

Titanium (Ti). The work developed by Noda et al.[58] showed that Ti electrodes possess no significant catalytic activity on their own for the electrochemical reduction of CO_2 in a $KHCO_3$ solution. However, TiO_2 has shown activity and has been used as an electrocatalyst with other metal oxides deposited onto the Ti substrate to catalyze CO_2 electroreduction.[92,94,96-99,120,121]

Monnier and collaborators reported the cathodic behavior of TiO_2, TiO_2/Ru and TiO_2/Pt thin film electrodes prepared by thermal deposition on Ti rods for the electrochemical reduction of CO_2.[120,121] Cyclic voltammetric measurements revealed adsorption of CO_2 in the TiO_2/Pt surface, which results in the formation of electrochemically detectable species. Lately, Bandi et al.[92,94] determined the Faradaic efficiency and current-voltage characteristics for the reduction of CO_2 on various conductive oxide mixtures (RuO_2, TiO_2, MoO_2, Co_3O_4, Rh_2O_3), resulting in higher current efficiencies for CH_3OH formation. It was concluded that the first electron transfer was the rate-limiting step in the reduction process in acidic media. As mentioned in the previous subsection, the study of CO_2 electroreduction at RuO_2-coated diamond electrodes showed that the main reduction products in acidic media were CH_3OH and HCOOH. The RuO_2-boron-doped diamond electrodes resulted in lower Faradaic efficiencies for CO_2 reduction to CH_3OH than when the substrate was replaced by a Ti material under identical conditions, concluding that the presence of TiO_2 enhances the formation.[96]

Moreover, Qu et al.[97] loaded RuO_2 onto TiO_2 nanotubes or nanoparticles, which were then coated onto a Pt electrode for the electrocatalytic reduction of CO_2. Compared with electrodes coated with RuO_2 or with RuO_2–TiO_2 nanoparticles, the electrodes coated with RuO_2–TiO_2 nanotubes had a higher electrocatalytic activity for the production of CH_3OH, with a current efficiency of up to 60.5%, which suggests that the nanotube structure is important in achieving a high efficiency and selectivity for CO_2 electroreduction. This finding has inspired the recent work of Li et al.[98] for the CO_2 transformation into CH_3OH at MoS_2-rods/TiO_2 nanotubes heterojunction electrodes with and without illumination application.

Mercury (Hg). The first trials on the electrochemical reduction of CO_2 at Hg electrodes were carried out by Teeter and Rysselbergue in 1954.[122] They demonstrated that the reduction proceeded principally to HCOOH. When the reduction of CO_2 was conducted in a neutral electrolyte at a Hg electrode, a high overvoltage and low efficiency for CO_2 reduction to HCOOH were observed.[123] Besides, HCOOH and CH_2O reductions to CH_3OH occurred with a Faradaic efficiency exceeding 90% in a basic solution at a current density of 10 mA·cm^{-2}. In any case, the application of Hg for the electroreduction of CO_2 has been substituted by other materials, in part for the significant pollution to the environment and adverse health effects that the release of this material may cause.

2.1.4. Noble metals

In contrast to other electrocatalytic materials, Pd and Pt have exhibited significantly different behavior towards CO_2

reduction, due to the differing interactions with adsorbed intermediates, such as CO or COOH, leading to different catalytic activities/stabilities and product selectivities depending on the way the material is applied.[124-127] Several works using electrodes based on Pt and Pd have resulted in the production of CH_3OH.

Platinum (Pt). In 1983, Eggins and McNeill studied the voltammetric reduction waves for CO_2 in water, dimethylsulphoxide, acetonitrile (which is not a recommendable solvent from an environmental point of view)[128] and propylene carbonate using electrodes based on Pt, among others.[129] Later on, Brisard et al.[130] used differential electrochemical mass spectrometry to investigate the reaction of electroreduction of CO_2 on Pt porous electrode. The results showed for the first time the production of CH_3OH in acidic media using a Pt electrodeposited electrode. The results also suggested that CO was the intermediate of the reduction pathway leading to CH_3OH.

Recently, Shironita et al.[131,132] investigated the CO_2 electroreduction at a carbon supported Pt (Pt/C) and Pt-Ru (Pt-Ru/C) electrode in a single cell to realize a CH_3OH-based reversible fuel cell. The electroreduction of CO_2 was shown to occur with a relatively high Faradaic efficiency of 30-50%. They speculated that the produced CH_3OH accumulates on the active site of the Pt/C electrocatalyst, reducing the reduction current with time. The CH_3OH yield efficiency was improved from 0.03% at the Pt/C to 7.5% at the Pt-Ru/C. Besides, the evaluated Faradaic efficiencies by cyclic voltammetry measurements were 35 and 75% at the Pt/C and Pt-Ru/C, respectively.

Palladium (Pd). Spichiger-Ulmann and Augustynski initiated in 1985 the study of CO_2 electroreduction in a 1.0 M $NaHCO_3$ solution at a Pd electrode.[133] A few years later, Azuma et al.[134] and Nagasawa et al.[135] concluded that the main products generated from the CO_2 electrocatalytic reduction were HCOOH and CO, and small amounts of hydrocarbons (from methane to hexane), in a $KHCO_3$ medium. It was also reported that the HER can be suppressed on the Pd surface, and so electrocatalytic activity can be enhanced.[136] Ohkawa et al.[137,138] modified a Pd electrode surface for the electrochemical reduction of CO_2 in aqueous $KHCO_3$ solution. The current efficiencies for CH_3OH, CH_4 and HCOOH production were larger on hydrogenated Cu-modified Pd electrodes than on non-hydrogenated electrodes. They hypothesized that the enhancement is caused by the participation of absorbed hydrogen in the reduction of CO_2, which was further explained by Podlovchenko et al. where CO and HCOOH were formed at low overpotentials, while a range of alkanes from methane to hexane were observed at higher potentials.[139]

2.1.5. Post-transition metals

Gallium (Ga) and Indium (In). In 1978, Halmann reported for the first time a photoelectrode made of a single crystal p-gallium phosphide (p-GaP) that was employed in an electrochemical cell to convert CO_2 into CH_3OH, C_2H_4 and HCOOH.[140] Based on these results, in 1983 Aurianblajeni et al.[141] and Canfield and Frese observed a high selectivity for the formation of CH_3OH in the electroreduction of CO_2 over semiconductors materials: gallium (p-GaP, p-gallium phosphide, p-GaP, and p-gallium arsenide, p-GaAs), and indium (p-InP) materials at lower current densities (<1 $mA\cdot cm^2$)[142-143]. The formation of CH_3OH was detected by GC/FID at both metals when using a CO_2 saturated-Na_2SO_4 electrolyte solution in a two-compartment cell separated by an agar bridge. The obtained selectivities for the production of CH_3OH (in the dark) were high (maximum 85%) at also high overpotentials at GaAs(111)-based electrodes. These high efficiencies encouraged the production of CH_3OH at these semiconductor materials.

Lead (Pb). In 1914, in one of the earliest studies on CO_2 electroreduction, Fischer and Prziza ran electrolytic reduction reactions of CO_2 dissolved under pressure in a steel bomb.[144] HCOOH was the major product obtained, although minimal amounts of CH_3OH were also obtained in K_2SO_4 and $(NH_4)_2SO_4$ electrolytes. Nevertheless, Pb presents a well-known toxicity, and an efficient CO_2 electroreduction process based on other green catalysis materials is preferred.

To summarize, the reported experimental data on the selective generation of CH_3OH from the electroreduction of CO_2, a lists of the data available in literature for the Faradaic efficiencies and CH_3OH production yields is presented as Supplementary information (Appendix II). The table includes the reaction medium, operation conditions and cell configuration in which the electrochemical reduction of CO_2 takes place. In general, the CO_2 transformation into CH_3OH at Cu, oxidized-Cu, and Cu/Zn-based electrodes seems to provide the highest Faradaic efficiencies and production yields among the reported materials.

2.2. Effect of the reaction medium on CO_2 reduction reaction

As previously discussed, the selection of the catalyst material is crucial for the selective production of CH_3OH from CO_2 electroreduction. However, the reduction mechanisms and reaction pathways (selectivity) and efficiency of the CO_2 electroreduction process are highly influenced by not only the metal surface. In fact, even for the same metal electrode with the same purity, different supporting electrolytes and operating conditions have been found to have a great effect on current density, product selectivity, and energetic efficiency in CO_2 reduction.[19,21,56,145-147]

In general, the electrochemical reduction of CO_2 commonly employs aqueous electrolytes consisted on alkali cations (e.g. Na^+, K^+) and various anions such as halide anions (e.g. Cl^-), bicarbonate (HCO_3^-) or hydroxide (OH^-) in aqueous solutions.[56,124,146,147] These inorganic salts are often used due to their high conductivities in water and because they can provide the required protons involved in the reaction pathway.

In 1986 Mo-based electrodes were pre-treated with HCl and applied for the electrochemical reduction of CO_2 in saturated aqueous solutions of 0.2 M Na_2SO_4 and 0.05M H_2SO_4.[91] Table 2 shows the Faradaic efficiency for the formation of CH_3OH on dependence of the CO_2-saturated electrolysis solution used.

Table 2. Faradaic efficiencies for CH_3OH production at Mo electrodes in 0.2 M Na_2SO_4 (pH= 4.2) or 0.05 M H_2SO_4 (pH= 1.5).

Electrolyte	T (ºC)	E (V vs. SCE)	j ($\mu A\cdot cm^{-2}$)	FE (%)
0.2 M Na_2SO_4	22	-0.70	26	42
	22	-0.80	50	55
0.05 M H_2SO_4	22	-0.68	310	46
	52	-0.60	590	21

As observed, the Faradaic efficiency for CH_3OH formation, at similar potential, was on dependence of the electrolyte solution applied. In the same work they reported an increased current efficiency (84%, electrolysis time: 23.3 h) when the electrodes where pre-treated with KOH or HF. Besides, in contrast to Ru electrodes,[93] the efficiency and product distribution on Mo-based cathode did not change much with the solution temperature even when raised to 52 ºC.

Schizodimou and Kyriacou evaluated the accelerating effect of various multivalent cations, the halogen anions and the acidity of the solution on the rate of the electrochemical reduction of CO_2 on a $Cu_{88}Sn_6Pb_6$ alloy cathode.[77] The rate of CO_2 electroreduction to CH_3OH increases with the increase of the surface charge of the cation of the supporting electrolyte in the order $Na^+ < Mg^{2+} < Ca^{2+} < Ba^{2+} < Al^{3+} < Zr^{4+} < Nd^{3+} < La^{3+}$ as observed in Figure 7.

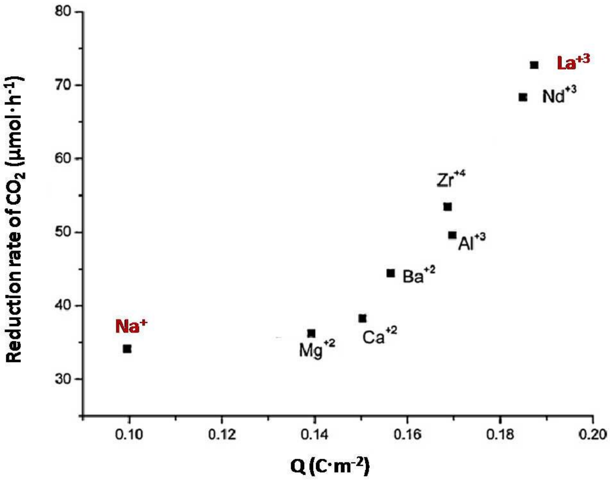

Figure 7. Rate of CO_2 reduction vs. surface charge of the cation at -0.69 (vs. SCE) in 1.5 M HCl solution containing various cations. Electrolysis time: 120 min. Reprinted from ref.[77], Copyright (2012), with permission from Elsevier.

The acceleration effect was attributed to the participation of the radical anion (CO_2^-) in the rate determining step. They also showed the generation of CO, HCOOH, CH_4 and CH_3CHO, together with CH_3OH, producing therefore a mixture that changed with the type of electrolyte and the cathode potential. The maximum current efficiency for CH_3OH was 28% at −0.60 V vs. SCE and they concluded that CO_2 reduction and the distribution of the products can be controlled simply by varying the composition of the electrolyte.

Other works evaluated the influence of the reaction medium for the formation of different products, although no CH_3OH was detected. For example in 1982 Hori and Suzuki conducted CO_2 electroreduction experiments on Hg electrodes, in one of the first reports on evaluating the effect of the reaction medium in the CO_2 reduction process.[148] Aqueous solutions of $NaHCO_3$, NaH_2PO_4–Na_2HPO_4, NaCl, $NaClO_4$, Na_2SO_4, $LiHCO_3$, and $KHCO_3$ and their combinations, were employed as electrolytes. The relationship between electrode behavior and solution properties were quantitatively clarified by the partial current densities of $HCOO^-$ formation and HER. Similar analyses were carried out by Eggins and McNeill in 1983 for the electroreduction of CO_2 on a Pt electrode in water, dimethylsulfoxide (DMSO), CH_3CN, and propylene carbonate solutions.[129] The apparent number of electrons involved in the reaction, and therefore the formation of different products, was determined from current densities in voltammetry and chronoamperometric analyses. Hori et al. studied in 1991 the electroreduction of CO_2 and CO with Cu electrodes in hydrogencarbonate solutions of various cations (i.e. Li^+, Na^+, K^+, and Cs^+) and observed that the product selectivity was importantly affected by cationic species as well as by HCO_3^- concentration.[146] H_2 formation prevailed over CO_2 reduction in Li^+ electrolyte, whereas CO_2 reduction was favorable in Na^+, K^+ and Cs^+ solutions. The selection of the cation influences the local pH (because of the different buffer capacities) at the Cu electrode and thus the nature and the amount of products formed. The main products were C_2H_4, CH_3CH_2OH and CH_4. The same author also reported the importance of anion choice (i.e. Cl^-, ClO_4^-, SO_4^-, HCO_3^-, $H_2PO_4^-$), which presented different buffer capacities, in the formation of reduced species from CO_2 electroreduction.[56] Similar to these findings, in 2012 Wu et al. found significant differences in activity and selectivity of Sn electrodes for $HCOO^-$ production when different electrolytes ($KHCO_3$, K_2SO_4, KCl, Na_2SO_4, Cs_2SO_4, $NaHCO_3$, and $CsHCO_3$) were used.[147] The results showed how the anion SO_4^{2-} and the cation Na^+ favor higher Faradaic efficiency and energy efficiency while HCO_3^- and Cs^+ enable a high rate production of $HCOO^-$.

Thorson et al. emphasized the significant role of the cation size ($Na^+ < K^+ < Rb^+ < Cs^+$) used in the reaction medium in the CO_2 electroreduction on Ag electrodes.[149] Specifically, they analyzed the effect of the alkali cations on the partial current densities of CO and H_2 products. The presence of large cations such as Cs^+ and Rb^+ in the electrolyte improves the partial current density for CO production, against H_2 formation. The effect of cation size on product selectivity for CO production can be explained by the interplay between the level of cation hydration and the extent of cation adsorption on Ag electrodes. Recently, Setterfield-Price et al.[150] investigated the influence of supporting electrolyte cations on the voltammetric behaviour and product distribution in N-methylpyrrolidone (NMP)-based CO_2 electroreduction systems at both Au and Pt electrodes. The results showed that when including TBA^+ (tetrabutylammonium) cations the current efficiency for CO_2 reduction was considerably larger than when Na^+, Li^+ or Rb^+ were present at high overpotentials. Besides, the system showed no evidence of deactivation.

In summary, the studies on the effect of the reaction medium on CO_2 electroreduction showed that:

(i) The selection of the anion may affect the local pH at the electrode and thus the availability of protons, which therefore influences reaction kinetics,

(ii) The size of the cation may influence its adsorption in the electrode surface, which greatly influences kinetics and the energy required in the reaction.

These considerations should be taken into account when choosing an appropriate electrolyte medium for the selective CO_2 electroreduction to CH_3OH.

In any case, the reported works generally conducted the electroreduction of CO_2 molecule in aqueous solution. However, the application of aqueous media in CO_2 electroreduction processes brings several drawbacks, such as:

(i) low selectivity for CO_2 reduction, since this reaction competes with HER in aqueous electrolytes,

(ii) slow reaction kinetics, which leads to an increase in overpotentials needed and costs,

(iii) formation of different byproducts that remain in the reaction medium, making the separation and recovery expensive and,

(iv) low solubility of CO_2 in water and surface contamination due to impurities in the electrolyte, which results in lower productivity.

2.2.1. Use of Solid Polymer Electrolytes (SPE)

In order to tackle the problems associated with the HER that entail a less efficient CO_2 electroreduction performance, the use of Solid Polymer Electrolytes (SPEs) has been proposed in literature. In these systems, CO_2 is directly provided as gas in the catholyte compartment and the SPE is responsible for the conduction of protons, separation of products gases and the electrical insulation of the electrodes. Although there are several reports that show the use of polymeric membranes to separate the liquid anolyte from the CO_2 saturated aqueous catholyte in divided cells[151-157], the literature on the use of SPE in which CO_2 is sent to the flow cell as gas is scarce.[131,132,158-162]

In 2012 Aeshala et al.[161] reported the formation of CH_3OH (with modest current efficiencies) after the electrochemical reduction of CO_2 in a reactor using Nafion/SPEEK/Amberlist. The prepared SPEs were characterized for thickness, thermal stability, ionic conductivity, and mechanical strength. An electrodeposited Cu coated on a carbon paper was used as cathode whereas Pt was used as anode. Other products from the reaction were mainly HCOOH, CH_2O, CO, and CH_4. In 2013, the same group studied the electroreduction of CO_2 at electrodeposited Cu_2O/carbon paper cathodes using cationic and anionic SPE.[162] Faradaic efficiency for the conversion of CO_2 into products was higher than 45% using the anionic solid polymer membrane at $5.4\ mA\cdot cm^{-2}$. The main products formed were CH_3OH, CH_4 and C_2H_4, apart from the undesired hydrogen gas as a by-product. They concluded that the SPE alleviated the mass transfer limitations of CO_2 in the electrochemical cell.

Other works reported the use of Cu-coated SPE prepared by electroless plating technique. When nafion was used as a cation exchange SPE, the electrochemical systems produced C_2H_4 as major product,[158,159] whereas the use of Selemion as anion exchange SPE produced CO and HCOOH.[160]

In conclusion, the use of SPE brings several advantages in comparison with the application of liquid electrolytes, such as:

(i) good tensile strength and ease of handling, which allow the fabrication of thin films and thus low resistance,

(ii) low convection, which reduces the problems of electrode erosion and increases the electrode life and,

(iii) easy separation of the reaction products.

Even if the current results are encouraging, further research is required to effectively use SPEs for the electrochemical transformation of CO_2 into CH_3OH in an improved electrochemical cell.

2.2.2. Other attempts to enhance CO_2 reduction

Several additional approaches have been experimentally demonstrated in literature to overcome the problems associated with the application of aqueous solutions, which are discussed hereafter.

Enzyme catalysts. In 1984, Parkinson and Weaver reported a novel approach for the fixation of CO_2 which combines a semiconductor electrode (indium phosphide, p-InP) with a biological catalyst (a formate dehydrogenase enzyme) for a two-electron reduction of CO_2 to HCOOH.[163] Kuwabata et al. carried out the electroreduction of CO_2 at potentials between -0.70 and -0.90 V vs. SCE phosphate buffer solutions (pH= 7) containing formate dehydrogenase (FDH) and either methyl viologen (MV^{2+}) or pyrroloquinolinequinone (PQQ) as an electron mediator yielded $HCOO^-$ with current efficiencies as high as 90 %.[164] Recently, Hansen et al.[165] developed a model based on density functional theory calculations to describe trends in catalytic activity for CO_2 electroreduction to CO, a CH_3OH formation intermediate, in terms of the adsorption energy of the reaction intermediates in the presence of carbon monoxide deshydrogenase enzyme. It was concluded that the active sites of the enzyme optimizes the binding energies of these adsorbates, allowing a reversible process with lower overpotentials needed.

Works that used enzyme catalysts for electroreduction of CO_2 to CH_3OH can also be found. The electrolysis of phosphate buffer solutions containing sodium formate in the presence of methanol dehydrogenase (MDH) and MV^{2+} at -0.70 V vs. SCE yielded CH_3OH and CH_2O at relatively high concentrations of the enzyme. The use of PQQ in place of MV^{2+} as the electron mediator exclusively produced CH_3OH alone after some induction period in the electrolysis. The enzyme was durable as long as the electrolysis was carried out in the dark. Addo et al. studied the role of carbonic anhydrase to efficiently facilitate uptake of CO_2, which can be the rate-determining step in the electrocatalytic production of CH_3OH from CO_2.[166] The three oxidoreductase enzymes responsible for CO_2 reduction to CH_3OH are formate, aldehyde, and alcohol-dehydrogenase. These enzyme cascades were coupled to a poly(neutral red) modified electrode to regenerate NADH, although they found that dehydrogenases alone can achieve reduction of CO_2. Furthermore, due to the presence of enzymes catalysts, the irreversible processes could become electrochemically reversible, as reported by Armstrong and Hirst.[167]

Metal complexes. There are several works in literature for the application of ES ($K_2FeII[FeII(CN)_6]$) and PB ($[Fe_4[Fe(CN)_6]_3]$) as an electron mediators when coated in the electrode surface. As discussed in section 2.2., several papers confirmed that CO_2 can be reduced to CH_3OH at ES-deposited electrodes and this reaction can be converted into a continuous process if the PB produced from ES during CO_2 reduction into CH_3OH is continuously reduced back to ES by continuous supply of electricity. [100-102,114-119,168] This reaction resulted in a reduced overpotential for the reduction of CO_2, although CH_3OH yields were still low. Based on the same principles, ES and PB have been applied as electron mediators in the reaction medium, as for example reported by Ogura and Takagi in 1986 where a mixture of KCl, CH_3OH and ES was used as an electrolyte.[119] The reduction of CO_2 from the current-potential curves denoted the formation of CH_3OH as the sole reduction production. From this study, it can be concluded that CO_2 could be reduced to CH_3OH using ES in the presence of a primary alcohol and a metal complex.

In any case, despite the fact that the use of enzyme catalysts and metal complexes significantly accelerate the rate of CO_2 reduction and product yields, in comparison to HER, high overpotentials for the reduction are still needed because of the low electrochemical efficiencies. The use of pyridinium molecular catalysts and ionic liquids in the reaction medium could be able to solve these overpotential problems to some extent.

Pyridinium molecular catalysts. In 1978, Raghavan and Iwamoto determined, in an electrochemical approach, the positions of coupling in the dimeric one-electron reduction products of 1-alkylpyridinium ions in acetonitrile.[169] The results suggested the properties of pyridinium as a selective molecular organic catalyst. One-year later pyridinium perchlorated was employed for voltammetric studies at several electrode materials (Pt, Pd, Au, Ti, Fe, Ni, Cd, Pb and Hg), in order to clarify the reduction mechanism of pyridiunium ion in acetonitrile, which is far to be considered a green solvent to be applied in an electrochemical process. Furthermore, in acidic electrolyte solutions, pyridine was found to undergo reduction to piperidine at a Pd electrode, generating also reduced CO_2 products.[170] The cyclic voltammetry study indicated that CO_2 electroreduction takes place at -0.55 V (vs. SCE) onset current. This corresponds to the thermodynamic potential for CH_3OH formation at pH= 5.4 (0.52 V vs. SCE).[171]

In the work developed by Seshadri et al. CO_2 was electrochemically reduced to CH_3OH using pyridinium solutions at Pd electrodes.[172] Although the reduction of protons to dihydrogen competes with CH_3OH, the Faradaic efficiency for CH_3OH was as high as 30%. They hypothesized that the reaction occurred at the electrode surface and also in the reaction medium, where pyridine and hydrogen were formed. As observed in Figure 8 the reduction of CO_2, or species in equilibrium with it, is promoted by species I to generate pyridine and reduced CO_2 products.

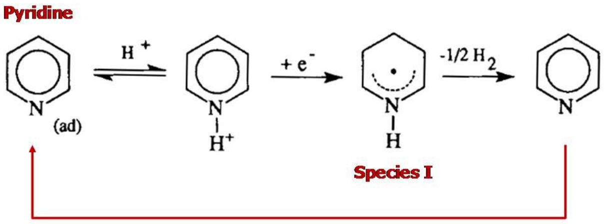

Figure 8. Schematic representation of pyridinium reduction coupled via electroreduction to the reduction of protons to hydrogen. Reprinted from ref.[172], Copyright (1994), with permission from Elsevier.

They also demonstrated that the formation of CH_3OH fell within a few hundred millivolts of the standard redox potential.[172] In 2010 Cole et al. reported the detailed mechanisms of pyridinium-catalyzed CO_2 electroreduction to CH_3OH when using a Pt disk electrode in a 10 mM aqueous solution of pyridine (Py) at low overpotentials (-0.58 V vs. SCE).[173] At the metal surface, HCOOH and CH_2O were observed to be intermediate products along the reduction pathway to CH_3OH, with the pyridinium radical playing a role in the reduction of both intermediate products.[174] In recent reports, Ertem et al. found that CO_2 is reduced by H atoms bound to a Pt surface that are transferred as hydrides to CO_2 in a mechanisms activated by pyridinium ($PyrH^+$).[175] Then, the surface bound H atoms consumed by CO_2 reduction is replenished by the one-electron reduction of $PyrH^+$, therefore generating reduced CO_2 products. In a theoretical study of CO_2 electroreduction in the presence of a pyridinium cation and its substituted derivatives, Keith and Carter reported the thermodynamic energies of various pyridine-derived intermediates using first principles quantum chemistry.[176] They concluded that the real form of the co-catalyst involved in pyridinium-based CO_2 reduction is not the long pyridinyl radical in solution, but that a surface-bound dihydropyridine species is more probable. In 2013, Lim et al. identified $PyCOOH^0$ as an important intermediate in the homogeneous CO_2 reduction by pyridine in a pyridine-p-GaP system. The formation of $PyCOOH^0$ was believed to be the rate-determining step for CO_2 reduction to CH_3OH. [177] Recently, Xiang et al.[178] demonstrated that 6,7-dimethyl-4-hydroxy-2-mercaptopteridine (PTE) acts as a molecular electrocatalyst for CO_2 reduction, without the involvement of any metal, at low overpotential. The FTIR spectroelectrochemistry analyses denoted a progression of two electron reduction products during bulk electrolysis, including $HCOO^-$, aqueous CH_2O, and CH_3OH. The efficiency for CH_3OH formation was in the range of 10-23%.

Other approaches have considered the application of polypyridyl transition metal complexes, such as $Re(bpy)(CO)_3Cl$ (bpy= 2,2′-bipyridine) or *cis*-$[(bpy)_2Ru(vpy)_2]^{2+}$ (vpy= 4-vinylpyridine) in order to overcome the high overpotentials needed in the electroreduction process.[179-182] In general, the results showed small increases in product yield for CO and HCOOH at low current efficiencies.

Ionic liquids. Ionic liquids (ILs) are molten salts with negligible vapor pressure and thermal stability above 200 °C and they are widely used in various fields of science.[183] Replacing the conventional aqueous systems with ionic liquids is advantageous for several reasons, which include the following:

(i) The HER, which competes for the reduction of CO_2, can be suppressed, [184]

(ii) The conductivity of the electrolyte can be enhanced due to the nature of charged ions, [185] and,

(iii) the solubility of CO_2 is higher than that in aqueous systems at a wide range of temperatures[186,187], thereby reducing mass transport limitations.

These are some of the key factors for an enhanced CH_3OH production.

There are some recent studies in literature that pointed out the potential application of ILs in the electroreduction of CO_2,[184,188-190] but none of them deal with the transformation of CO_2 to CH_3OH. For example, in 2011, Rosen et al. reported an electrocatalytic system that reduces CO_2 to CO at overpotentials below 0.20 V (vs. SCE).[184] The system relies on an 1-ethyl-3-methylimidazolium tetrafluoroborate, [emim][BF_4] ionic liquid electrolyte to lower the energy of the CO_2^- intermediate, which is the responsible for the large overpotentials associated with electrochemical CO_2 reduction. First, [emim][BF_4] appears to convert CO_2 into CO_2^- intermediate, which is then catalysed over a silver cathode to form CO. The CO product was formed at -250 mV overpotential in comparison to -800 mV in the absence of the ionic liquid. The system continued producing CO for at least 7 h at Faradaic efficiencies greater than 96%. Therefore the CO_2 conversion to CO can occur without a large energy loss associated with a high overpotential. In further works, [191] it was observed that the addition of water to [emim][BF_4] increased the efficiency of CO_2 conversion to CO as observed in Figure 9. They attributed this increase to the hydrolysis of tetrafluoroborate, which releases protons when mixed with water.

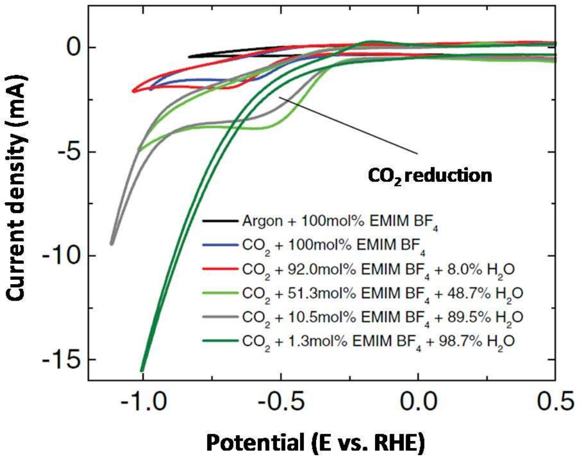

Figure 9. Effect of adding water to [emim][BF_4] on CO_2 reduction on a Ag-based electrode (v= 50 mV·s^{-1}). Potential vs. RHE. Reprinted from[191], Copyright (2013), with permission of The Electrochemical Society.

Dimethyl carbonated (DMC) is a product whose electrosynthesis from CO_2 and methanol with the use of ILs has been focus of increasing attention. For example, an amino-functionalized ionic liquid, 1-(3-aminopropyl)-3-methylimidazolium bromide ([Apmim][Br]) was used as electrolyte in the electrochemical activation of CO_2 and synthesis of DMC using graphite electrode at ambient pressure and temperatures.[189] The high selectivity obtained (95%) was ascribed to the basicity of the IL, which was advantageous for capturing the CO_2 molecule. Besides, I. Garcia-Herrero et al. quantified the direct electrosynthesis of DMC from CO_2 and CH_3OH using a CH_3OK and [bmim][Br] ionic liquid solution in a filter-press electrochemical reactor.[192] A final DMC concentration of 15.07 mmol·L^{-1} was observed, concluding that the IL was not merely an electrolyte, but a required substance to obtain the desired product.

A further understanding on the mechanisms underlying the electroreduction of CO_2 in the presence of an IL is still required in order to improve the efficiency for the transformation of CO_2 into useful products, which in turn could be applied to the specific case of producing CH_3OH.

2.3. Effect of operating conditions

Despite the fact that operating conditions may highly influence yields and product selectivities only a few reports to date have focused on evaluating the effect of pH, temperature and pressure on the CO_2 electroreduction performance.[19,21] In the case of CO_2 electrocatalytic conversion to CH_3OH, this evaluation is practically unexplored yet.

2.3.1. Effect of pH

Neutral or slightly acid media are generally applied in the electrochemical reduction of CO_2, since CO_2 cannot survive in basic solutions. However, with decreases in pH, the HER is thermodynamically preferred in comparison to the reduction of CO_2. Besides, CO_2 reduction reactions lead to the formation of OH^-, making the pH in the vicinity of the electrode surface to be higher when compared with the rest of the solution pH.[193] As high pH conditions do not favor CO_2 reduction, electrolytes with buffering properties such as $KHCO_3$ or K_2HPO_4 are normally employed, as they can supply anions that can serve to diminish the pH changes occurred during reaction at the electrode surface.

Several reports can be found in literature for the effect of pH in the electroreduction of CO_2.[19,21,56,77,91,93,96,146,193,194] For example, in one of the first studies on CO_2 electroreduction kinetics, Paik et al. reported the reduction of CO_2 to HCOOH at Hg electrodes in buffered neutral and acidic aqueous solutions and determined the resultant current efficiencies.[194] They found that in the neutral pH range all the current is consumed in the production of HCOOH, while in acid solutions both HCOOH and also H_2 were formed, since the reduction of CO_2 occurred in parallel with the reduction of H_3O^+ ions to yield H_2. Focusing on studies that involved the production of CH_3OH, Frese et al. patented a method for producing CH_3OH from CO_2 in aqueous solvents utilizing Mo-based cathodes.[91] The current density and Faradaic efficiencies reached in the system were clearly enhanced when using 0.05 M H_2SO_4 (pH= 1.5) as an electrolyte, in comparison to the application of 0.2 M Na_2SO_4 (pH= 4.2) solutions. In 2003, carbon dioxide reduction studies were conducted at RuO_2-coated diamond electrodes in acidic media, mainly producing CH_3OH with a 7.7% current efficiency. It was found that the efficiency for hydrogen formation is higher than 50% only at pH= 2.4, while at higher pH values CO_2 reduction prevails.[96] The highest efficiencies for the electrochemical reduction of CO_2 were obtained at a pH≈ 3.9. In 2012, Schizodimou and Kyriacou tested various multivalent cations and the acidity of the electrolyte solution on the electroreduction of CO_2 at Cu alloys.[77] The obtained results presented in Table 3 indicated again that with decreases in pH of the reaction medium, the rate of CO_2 reduction to CH_3OH importantly increases, with enhancements in current density at both -0.75 and -1.70 V applied potentials.

Table 3. Faradaic efficiency for CH_3OH production and total CO_2 reduction rate, *r*, in a 0.01M CH_3COOH solution containing various cations. Electrolysis time= 120 min.

Electrolyte	pH	FE (%)	Charge (C)	r (10^{-6} mol·h^{-1})
at -0.75 V				
0.01 M CH_3COONa	4.53	10.2	14.82	22.82
0.003 M $BaCl_2$	4.56	7.9	19.56	29.48
0.0016 M $LaCl_3$	4.14	7.1	48.36	65.84
0.05 M $LaCl_3$	4.02	6.7	49.11	69.77
at -1.70 V				
0.01 M CH_3COONa	4.53	0.5	300.46	84.96
0.0016 M $LaCl_3$	4.14	0.8	315.52	93.37

2.3.2. Effect of temperature

The product distribution in the CO_2 electroreduction process is strongly influenced by reaction temperature. In 1985, Frese demonstrated the important effect of temperature on CO_2 electroreduction conversion to CH_3OH when using a Ru-teflon electrode in 0.2 M Na_2SO_4 at pH= 4-7.[93] The Faradaic efficiency was as high as 42% at 60 ºC. The important effect of temperature was further demonstrated when evaluating Mo-based electrodes at 22 ºC and 52 ºC (Table 2).[91]

Hori and co-workers carried out gavanostatic work over a temperature range from 0 to 40º C.[50] The results denoted an increased Faradaic efficiency of 65% for CH_4 formation at 0 ºC. The same effect was observed by Azuma et al.[75], when comparing the efficiencies for CO_2 electroreduction at a temperature of 0 to 20 ºC in 0.05 M $KHCO_3$ at -2.2V vs. SCE, or by Kaneco et al. in 2002, where potentiostatic experiments (-2.0 V vs. SCE) in 0.65 M $NaHCO_3$ over the temperature range from 2 to 15 ºC were conducted.[195] The hydrogen formation was significantly depressed with decreasing temperature. The same tendency was observed in other works where an increase in CO_2 reaction rates at 0 ºC ($3.06 \cdot 10^{-4}$ mol·m^{-2}·s^{-1}) in comparison to those values at 22 ºC ($2.22 \cdot 10^{-4}$ mol·m^{-2}·s^{-1}) on Cu foil electrodes in 0.5 M $KHCO_3$ were observed at a current density range of 17-23 mA·cm^{-2}.[52] These results suggest that lower temperatures influence adsorption equilibrium and increase CO_2 solubility, where the electrochemically assisted dissociation of adsorbed CO by electron transfer is suggested as the rate determining step. Similar results were obtained by Shironita et al. when calculating Faradaic efficiencies and detected CH_3OH yields in the exhausted gas from a reversible fuel cell at 26-90 ºC temperature range.[130]

2.3.3. Effect of pressure

The experimental evaluation of the effect of the effect of pressure on CH_3OH formation from CO_2 electroreduction is almost unexplored yet.

The utilization of CO_2 in aqueous solutions can be limited by the low solubility of CO_2 in the reaction medium. To speed up the reaction process pressurized CO_2 is usually applied, which often causes a certain degree of change in product selectivity.[196-198] For example, Hara et al. increased CO_2 pressure from 0 to 60 atm, and run galvanostatic experiments at a Cu wire cathode.[196] Increases in CO_2 pressure produced the predominant reaction to shift from hydrogen to hydrocarbons, reaching 44% current efficiency by around 10 atm of CO_2. Nevertheless the results showed that hydrocarbons can be produced at close to 60% current efficiency at 600 mA·cm^{-2}, which is important for any practical CO_2 conversion reactor. The same group applied several electrode materials at large current densities (163-700 mA·cm^{-2}) for CO_2 electrochemical reduction at 30 atm pressure in $KHCO_3$ solutions.[198] The total current density on the cathodic voltammograms of Ag, Au, Zn, Pb and In metal electrodes increased with increasing CO_2 pressure from 1 to 30 atm, resulting in HCOOH and CO. On the other hand, in Fe, Co, Rh, Ni, Pd and Pt electrodes, the main reduction products were HCOOH and CO under high pressure, whereas, under 1 atm CO_2, H_2 was formed by reduction of water. In these cases, the total current density changed only slightly with increasing CO_2 pressure.

In 2002, Aydin and Köleli reported the electroreduction of CO_2 at the low overpotential value of -0.40 V vs. SCE on polyaniline (PAn) electrodes under high pressure in a CH_3OH-$LiClO_4$ electrolyte.[199] When increasing pressure, the current density increases gradually in the system. The maximum Faradaic efficiencies are found to be 26.5, 13.1 and 57 % for HCHO, HCOOH and CH_3COOH formation, respectively.

2.4. Design of the electroreduction cell

2.4.1. Types of electrochemical cells

From literature, it can be observed that different research groups have used a variety of flow or electrolyzer configurations for CO_2 electroreduction.[200-204] There is not a standard cell configuration or methodology for studying the electroreduction of CO_2 to CH_3OH. Most of the published studies for the electrocatalytic conversion of CO_2 to CH_3OH have reported the use of two-compartment electrochemical cell configuration,[77,85,89,92,93,96-98,107-110,131,132,154] in comparison to the traditional undivided three-electrode electrochemical cells.[64,67,69,90,94,95,98] In the divided systems, the cathode and anode compartments are generally separated by a Nafion exchange membrane,[41,45,77,780,84,89,96,97,99,100,110,131,132,161,162] Na_2SO_4 or an agar bridge,[93,142] and a glass frit.[100,102,107,172] The use of other configurations, such as membrane electrode assemblies (MEA) has been used for CO_2 conversion to CH_3OH in only a few reports.[131,132,160,161] Figure 10 shows some examples of divided cell configurations, where the working and counter electrodes are separated by an ion exchange membrane.

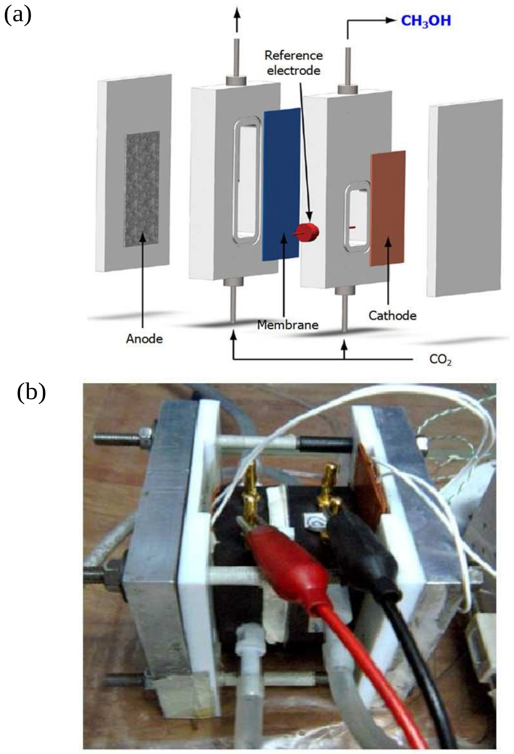

Figure 10. (a) Schematic representation and (b) photograph of an electrochemical cell divided by an ion exchange membrane. Fig 10a is reprinted from ref.[45] and Fig 10b is reprinted from ref.[161], Copyright (2012), with permission from Elsevier.

Jhong et al. suggested that even if the cell configuration might have a profound effect on mass transport, apparently is not the limiting step in the electroreducion performance of CO_2.[28] If that is the case, the structure and configuration of the catalytic surface in the electrode may play a vital role in the electrochemical reactions for CO_2 conversion.

2.4.2. Structure of the electrode

Metallic electrodes applied in CO_2 electroreduction processes can be basically classified into the following types:
(i) bulk metal (plate, foil, etc.) electrode,
(ii) metals electrodeposited in a metallic/glassy carbon support (GCE) or,
(iii) metals supported in gas diffusion electrodes (GDE).

In general, the electrodes types (ii) and (iii) comprised a catalyst layer and a support that serves firstly to deliver CO_2 from flow channels to the catalytic sites, secondly to transport the reduced product from the catalytic sites into flow channels, and finally, to conduct electrons with low resistance.[204,205] Therefore, maximizing electrode performance, and consequently reactor performance, requires optimizing all of the transport processes that strongly depend on the structure of the electrode. Only a few reports to date, however, can be found in literature for the analysis of the relation of electrode structure and the performance of electrochemical processes.[64,124,201,206-208] For example, Frese analyzed the CO_2 reduction to CH_3OH at various Cu foil electrodes (i.e. anodized Cu foil, Cu foil thermally oxidized and air-oxidized Cu foil). Faradaic yields for CH_3OH depended on the current and reached about 240 % in 0.5 M $KHCO_3$, pH= 7.6, and -1.9 V (vs. SCE).[64] In 1994, Hori et al. evaluated the performance of CO_2 electroreduction using planar metal electrodes (i.e. Cu, Zn, Pd, Ga, Pb, Hg, In, Sn, Fe, Pt, Ti, etc.) at low current densities ($5\ mA\cdot cm^{-2}$).[124] The low surface area, together with the low concentration of CO_2 at the electrode surface due to reduced CO_2 solubility in aqueous solutions, led to a limited performance of planar electrodes. In 2011, Le et al. examined the yield for CO_2 transformation into CH_3OH of an electrodeposited cuprous oxide thin film.[69] They explored the relationship between surface chemistry and reaction behavior relative to air-oxidized and anodized Cu electrodes in an undivided three-electrode cell. The high CH_3OH conversion rates ($1.2\cdot 10^{-4}\ mol\cdot m^{-2}\cdot s^{-1}$) and Faradaic efficiencies (38%) were remarkably higher in electrodeposited electrodes than in air-oxidized or anodized Cu electrodes. Furthermore, Bandi et al. prepared Ru/TiO_2 catalysts in rotating disk electrodes.[94] An analysis of the electrode kinetics for the formation of reaction intermediate suggests that the surface recombination of adsorbed hydrogen with CO_2 is the rate-limiting step in the electrochemical reduction of CO_2. As the current efficiency depends of the continuous removal of the products obtained (CH_3OH, $HCOOH$ and CH_3CH_2OH) from the electrode surface, the use of these electrodes is recommended. Chang et al. synthesized Cu_2O particles that were dispersed (brush-painted) on carbon clothes for electrochemical characterizations (i.e. cyclic voltammetry and potentiostatic measurements) in a CO_2 saturated 0.5 M NaOH solution contained in a three-electrode undivided cell.[67] The material presented notable catalytic ability for the CO_2 reduction with CH_3OH as the predominant product.

Recently, the application of GDE for electrochemical processes is concentrating the CO_2 electroreduction research efforts.[84,161,162,209] A GDE is a porous composite electrode usually composed of polymer bonded catalyst particles and a carbon support. To date, researchers have reported moderate to high current densities ($200\text{-}600\ mA\cdot cm^{-2}$) in mild conditions[4] or under pressurized electrolyzer systems ($300\text{-}900\ mA\cdot cm^{-2}$).[210] Schwartz et al. firstly studied perovskite-type crystal structures ($A_{1.8}A'_{0.2}CuO_4$, A= La, Pr and Gd; A´= Sr and Th) in GDE for the electrochemical reduction of CO_2 under ambient conditions.[209] The results showed that perovskite-type electrocatalysts could achieve cumulative Faradaic efficiencies for CO_2 reduction to CH_3OH, CH_3CH_2OH, and C_3H_8O up to 40% at current densities of $180\ mA\cdot cm^{-2}$.

In the literature for the production of other useful products, Delacourt et al.[200] and Jhong et al.[206] recently prepared (by hand-painting or spray-painting methods) GDE electrodes with Ag catalyst inks with current densities as high as $91\ mA\cdot cm^{-2}$ in combination with 94% Faradaic efficiency for CO formation using a microfluidic cell in which a flowing aqueous KCl electrolyte separated the cathode and Pt anode. The energetic efficiency was as high as 46%.[206] Besides, the deposition of the catalyst using an airbrushing method yielded a very thin, crack free layer, reducing at the same time the amount of metal needed compared to other type of electrodes. Del Castillo et al. studied the influence of key variables in the continuous electroreduction of CO_2 to $HCOO^-$ at GDE loaded with Sn.[211] The results showed higher rates and concentration of $HCOO^-$ (i.e. $1.4\cdot 10^{-3}$ mol $m^{-2}\cdot s^{-1}$, 1348 mg·L^{-1} and a Faradaic efficiency of 70%) than those results on planar electrodes, showing that GDEs are advantageous for these electrochemical CO_2 reduction reactions. Furthermore, Salehi-Khojin et al. investigated the effect of particle size on CO_2 reduction activity.[212] They concluded that the production of CO from CO_2 electroreduction was enhanced when decreasing particle size from 200 to 5 nm.

In summary, the use of GDE in combination with optimized catalyst layer deposition methods lead to significant improvement in the performance of CO_2 electroreduction. This electrode structure, together with the use of SPE, have solved certain problems associated with the use of liquid phases in the electroreduction of CO_2 and improved the mass transfer of CO_2.[54,197,198,210,212,213] However, despite the promising results of GDEs, further research is required to optimize chemical composition of the catalyst layer (e.g. pore size and distribution, binder material, etc.) and porous support (e.g. thickness, porosity, etc.) impact the transport of CO_2 and the generated products.

3. Comparison with different electrocatalytic routes

As discussed through the review, the electroreduction of CO_2 can be performed under different conditions, leading to the formation of several compounds. In order to compare the electrocatalytic route for CO_2 reduction to CH_3OH with those for obtaining other products, Figure 11a and 11b show, respectively, the Faradaic efficiency (selectivity of the process for a given product) and the energy efficiency (total energy used toward the formation of the desired product) against the current density applied in the process, for the electrochemical conversion of CO_2 to CH_3OH. The results are compared to CO and HCOOH formation routes, which are among the most common products formed from the reduction of CO_2.

The Faradaic (FE) and energy efficiencies (EE) can be calculated according to equation 1 and 2, respectively:

$$FE(\%) = \frac{z\cdot n\cdot F}{q}\cdot 100 \qquad (1)$$

$$EE(\%) = \frac{E_T}{E}\cdot FE \qquad (2)$$

In equation 1, z is the number of e^- exchanged to formed the desired product, n is the number of moles produced, F is the Faradaic constant (F= 96,485 C·mol^{-1}) and q is the total charge applied in the process. For the energy efficiency (equation 2), E_T stands for the theoretical potential needed in the electrochemical system for the formation of the product of interest, while E represents the real potential applied in the process. It is clear, that higher energetic efficiencies can be obtained when high FE and low overpotentials on the cathode can be obtained.

It should be noted that the figures uniquely provide a picture of the technical and economic feasibility of the different electrocatalytic routes, although the data come from studies where different variables, namely cathode materials, reaction medium, operating conditions and/or cell/electrode structure, affect the results. The extraordinary high Faradaic efficiency data obtained for CH_3OH formation (i.e. >100%), where clearly both chemical and electrochemical steps are involved in the CO_2 reduction process, have been removed in order to clarify the analysis. Values for CO and HCOOH formation come from several reported values published in literature.[16,32,176,202,214-222]

In general, electrocatalysts for the CO_2 reduction to CO are based on Au, Ag, Zn, Pd and Ga metals, while for HCOOH, Pd, Hg, In, Sn, Cd and Tl resulted more active.[32]

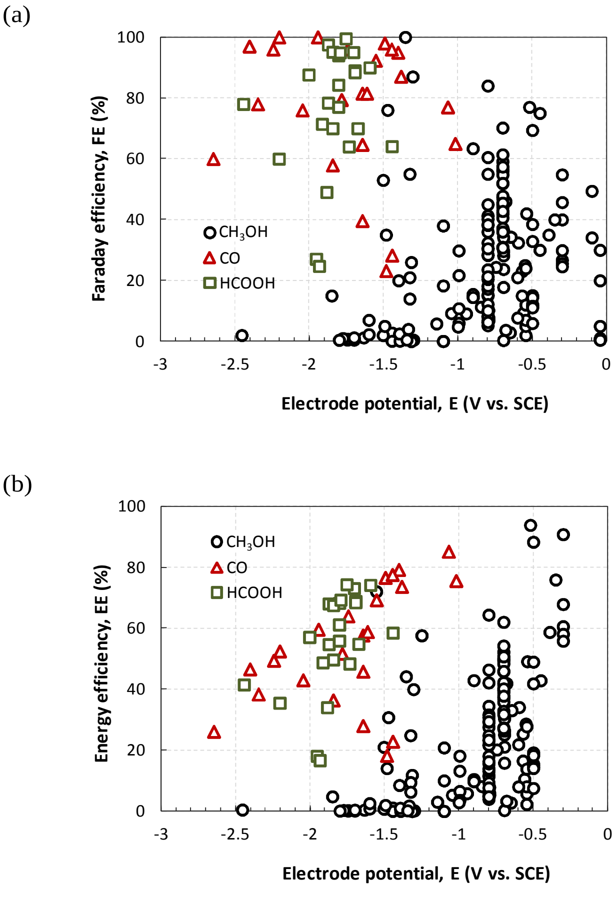

Figure 11. Comparison of (a) Faradaic efficiency and (b) energy efficiency against current density for CO_2 conversion into CH_3OH, CO and HCOOH.

As observed, electrochemical processes for CO_2 transformation into CH_3OH usually offer lower Faradaic and energy efficiencies at lower applied voltages, in comparison to CO and HCOOH electrocatalytic routes. That means that further work is still required to improve significantly the selectivity and optimizing the total energy required (avoiding energy losses in the process) for the transformation of CO_2 to CH_3OH, before it can be implemented in industry for a zero CO_2 emission-based economy.

3.1. Considerations about the energetic aspects of the process

An evaluation of not uniquely the electrocatalytic CO_2 reduction reaction, but also an economic viability and a critical environmental sustainability evaluation (by means of the life cycle assessment methodology) of the integrated process is required in order to achieve a feasible electroreduction system. Other key issues, such as the CH_3OH concentration, the energy duties in the separation step, as well as the primary energy sources for the conduction of the CO_2 reduction reaction should be analyzed and take into account.

The methanol concentration values reported in the literature for CO_2 electroreduction processes ranged from 0.04 to 202.24 $mg \cdot L^{-1}$, as shown in Supplementary information (Appendix II). Obviously, even concentrations in the order of 200 $mg \cdot L^{-1}$ will request a large amount of energy in the separation step. These energy requirements will be, of course, in line with the industrial purity requirements for the obtained products. In a first attempt to evaluate the environmental sustainability for the CO_2 electroreduction to HCOOH, an approximately 5 times higher energy consumption was estimated for the separation step in the distillation column (input feed concentration of 1 M/46,000 $mg \cdot L^{-1}$), in comparison to that energy required for the CO_2 electroreduction reaction itself.[34] The integration of renewable energies and alternative purification process, instead of conventional distillation, are therefore required to ensure a process with a reasonable energy profile. In this regard, the use of SPE, where CO_2 is directly provided as gas in the catholyte compartment, may also help to achieve an easier separation of methanol from other reaction products, improving, at the same time, the reactant mass transfer process.

The same study also identified the lifetime of the electrodes as a critical process parameter.[34] Lifetime in the order of thousands of hours is needed in order to have a potentially viable process with an environmentally beneficial profile, or else, a regeneration technique for the electrodes with minimal consumption of energy and chemicals.

4. Concluding remarks and future perspectives

The electrocatalytic reduction is one of the most promising technologies for CO_2 recycling, dealing with the depletion of fossil fuels and global warming issues. Compared with other technologies for CO_2 mitigation, such as sequestration for example, the electrochemical valorisation is an environmentally sustainable option which gives the possibility to close the loop and generate useful products from CO_2, storing electricity in different chemicals. Besides, this process can be carried out at mild conditions. Among the different liquid fuels and useful chemicals from CO_2 electroreduction, CH_3OH is particularly interesting. This review paper gives a clear picture of several decades of research on CO_2 electrochemical transformation to CH_3OH, analyzing the effect of catalysts materials, electrolytes and cell/electrodes configuration in the reaction efficiency.

The formation of CH_3OH is known to occur at several types of electrocatalysts, where the oxidized Cu-based electrodes seem to be the most promising materials in terms of combined, product selectivity and current efficiency. Despite all the efforts put into electrochemical CO_2 reduction, the production of CH_3OH seems to be still far from practical applications, although with continued and extensive efforts the technology of CO_2 electroreduction will become practical and economically feasible in the near future.

There are several issues that need to be tackled for this technology to achieve widespread use:

4.1. Development and application of new cathode materials

In order to achieve industrial-scale implementation, one of the main challenges is the stability of the electrode material, but scarce long-term tests have been done in literature. The reaction intermediates and by-products may poison and block the active sites in the catalysts, leading to a catalytic deactivation. The development of stable materials, with high activity and selectivity, is a priority. Nevertheless, a continuous steady formation of CH_3OH at high current densities is yet to be seen.

4.1.1. Enhancing catalyst activity and product selectivity

The transformation of CO_2 to liquid fuels and useful chemicals will require new methods and approaches for activating the CO_2 molecule at lower overpotentials. The research efforts may focus on new complex catalysts and catalyst assemblies, including hybrid metal catalysts, nanostructures (nanotubes/spheres/sheets, etc.) and MOFs, which may probably lead to promising catalysts activity, reducing overpotentials needed. It is crucial to focus on the precise tuning of the electrode surface area, catalysts morphologies, composition of multi-metal electrodes, actives sites and porosity of the support layer, which facilitates the diffusion pathways and lead to faster kinetics, an efficient electron and proton conduction and accessible active sites for the catalytic process.

Today, only a few attempts have explored the application of these new materials for the electroreduction of CO_2 to CH_3OH. For the majority of the catalysts reported in literature, even if they show moderate activity, the product selectivities are still low, and some undesired products are also formed.

4.2. Development and application of new electrolytes

The high overpotentials for the CO_2 electroreduction process are related to the hydrogen evolution reaction (HER), which competes with the formation of CH_3OH. The literature offers some examples where higher Faradaic efficiencies could be achieved using catalysts with low hydrogen overpotentials in combination with electrolytes that minimize or suppress the formation of hydrogen. Besides, the solubility in the reaction medium is one of the controlling factors in CO_2 conversion, because of the effects on mass transfer. Therefore, a fine-tuning of the electrolyte composition for a given catalyst offers a further opportunity for performance enhancements.

There is a great potential for conversion improvements in the application of pyridine solutions or non-aqueous media, such as ionic liquids. The application of ionic liquids for CH_3OH formation from the electroreduction of CO_2, however, is still not reported, and therefore great research efforts are still required. Besides, the application of Solid Polymer Electrolytes (SPE) developed in recent years seem to be one alternative for reducing internal resistance and improving the reactant mass transfer process.

4.3. Development and application of new cell/electrode configurations

In the future, the research should also deal with the design of electrolysis cells and electrode structures, including the assembly of membranes to separate cell compartments. There are scarce reports to optimize systems design, although the structure of the electrode seems to be a particularly important challenge in order to enhance current density and CO_2 transfer to the electrode surface in the system.

A key opportunity resides in the application of the so-called Gas Diffusion Electrodes (GDE), which creates a three-phase interface between the gaseous reactants, the solid catalyst, and the electrolyte, improving current densities and reducing overpotentials needed. The future research should probably include the relation of GDE morphology with an effective gas-liquid separation, while facilitating transport of reactants and products. These efforts will help to achieve the scale-up of CO_2 recycling processes and devices in continuous operation.

4.4. Further understanding of the reaction mechanisms

The understanding of the CO_2 reaction mechanisms (C-O, C-C and C-H bonds formation), pathways and intermediates to generate useful products is still insufficient, although the literature contains some attempts to understand the CO_2 electroreduction process through both experimental and theoretical modelling approaches. Such efforts in fundamental mechanistic studies will guide the development of new catalysts and the optimization of operation conditions.

Finally, the estimation of the actual costs to produce CH_3OH via electrochemical reduction of CO_2 will require the development of in-depth cost and life cycle analysis models.

Acknowledgements

The authors gratefully acknowledge the financial support from the Spanish Ministry of Economy and Competitiveness (MINECO), under the project ENE 2010-14828, CTQ2013-48280-C3-1-R and *Juan de la Cierva* program (JCI-2012-12073).

Notes and references

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† Electronic Supplementary Information (ESI) available: List of review articles on CO2 electrochemical transformation into useful products (Appendix I) and, summary of the best performance data for the electrocatalytic reduction of CO_2 to CH_3OH (Appendix II). See DOI: 10.1039/b000000x/.

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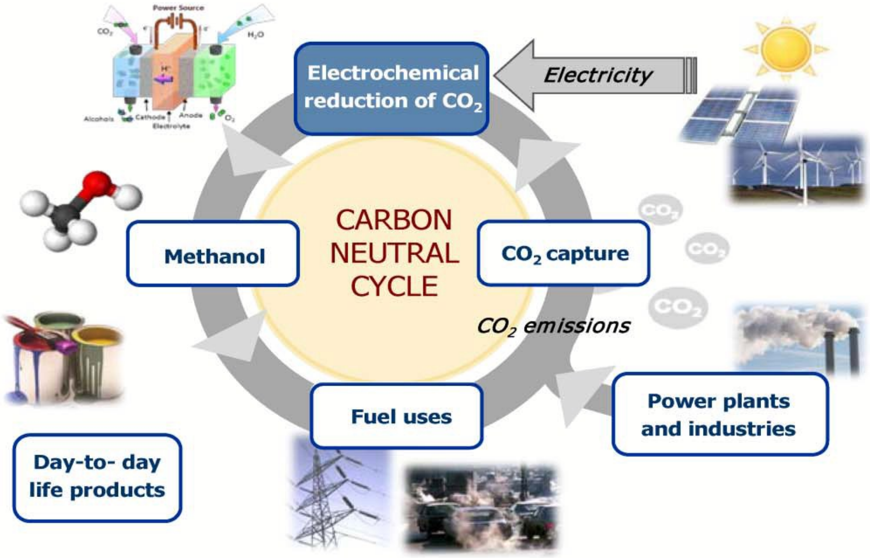
Graphical abstract



Electrocatalysis for carbon dioxide conversion into methanol

Electronic Supplementary Information (ESI)

Appendix I.

List of review articles on CO_2 electrochemical transformation into useful products.

Author (year)	Publication title	Ref.
A. F. Sammells et al. (1993)	Electrochemical and electrocatalytic reactions of carbon dioxide	[A.1]
M. Jitaru et al. (1997)	Electrochemical reduction of carbon dioxide on flat metallic cathodes	[A.2]
C. M. Sánchez-Sánchez et al. (2001)	Electrochemical approaches to alleviation of the problem of carbon dioxide accumulation	[A.3]
R. P. S Chaplin and A. A. Wragg (2003)	Effects of process conditions and electrode material on reaction pathways for carbon dioxide electroreduction with particular reference to formate formation	[A.4]
M. Gattrell et al.(2006)	A review of the aqueous electrochemical reduction of CO_2 to hydrocarbons at copper	[A.5]
M. Jitaru (2007)	Electrochemical carbon dioxide reduction- fundamental and applied topics (review)	[A.6]
Y. Hori (2008)	Electrochemical CO_2 reduction on metal electrodes	[A.7]
E. E. Benson et al.(2008)	Electrocatalytic and homogeneous approaches to conversion of CO_2 to liquid fuels	[A.8]
J. Lee et al.(2009)	Electrocatalytic recycling of CO_2 and small organic molecule	[A.9]
W. Li (2010)	Electrocatalytic reduction of CO_2 to small organic molecule fuels on metal catalyst	[A.10]
D. T. Whipple and P. J. A. Kenis (2010)	Prospects of CO_2 utilization via direct heterogeneous electrochemical reduction	[A.11]
G. Centi and S. Perathoner (2011)	CO_2-based energy vectors for the storage of solar energy	[A.12]
N. S. Spinner et al.(2012)	Recent progress in the electrochemical conversion and utilization of CO_2	[A.13]
Y. Oh and X. Hu (2013)	Organic molecules as mediators and catalysts for photocatalytic and electrocatalytic CO_2 reduction	[A.14]
H. R. Jhong et al.(2013)	Electrochemical conversion of CO_2 to useful chemicals: current status, remaining challenges, and future opportunities	[A.15]
J. P. Jones et al.(2013)	Electrochemical CO_2 Reduction: Recent advances and current trends	[A.16]
E. V. Kondratenko et al.(2013)	Status and perspectives of CO_2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes	[A.17]
R. J. Lim et al. (2014)	A review on the electrochemical reduction of CO_2 in fuel cells, metal electrodes and molecular catalysts	[A.18]
J. Qiao et al.(2014)	A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels	[A.19]

Appendix II.

Summary of the best performance data for the electrocatalytic reduction of CO_2 to CH_3OH. Potential values (*E*) have been converted to SCE reference electrode and current density (*j*) in $mA \cdot cm^{-2}$.

Electrode	Electrolyte/Cell configuration	E (V vs. SCE)	Current density ($mA \cdot cm^{-2}$)	Concentration ($mg \cdot L^{-1}$)	Reaction rate (10^{-6} $mol \cdot m^{-2} \cdot s^{-1}$)	FE (%)	Ref.
Cu-based electrodes							
Pre-oxidized Cu foil (1 h, 130 ºC)	0.5M $KHCO_3$/Undivided	-0.05	0.069	-	3.61 x $10^{-3\ a}$	~240	[A.20]
Pre-oxidized Cu foil (17 h, 130 ºC)		-1.55	7.1	-	23.6^{a}	-	
Anodized Cu foil		-1.25	1.4	-	27.8^{a}	~120	
Pre-oxidized Cu-TiOx (50 min., 300 ºC)		-1.06	0.74	-	22.5^{a}	~180	
Pre-oxidized Cu-TiOx (45 min., 500 ºC)		-0.45	0.30	-	33.3^{a}	~30	
Perovskite ($La_{1.8}Sr_{0.2}CuO_4$) based carbon GDE	0.5M KOH/ Two compartments (Nafion 117)	-2.30 to -2.60	180	-	-	2	[A.21]
Air-furnace oxidized Cu	0.5M $KHCO_3$/Undivided -Three electrodes	-1.50	~10	$0.12\text{-}0.25^{a}$ (10 min)	1.94^{a}	2	[A.22]
Anodized Cu foil (Electrochemically oxidized)		-1.40	~5	$0.20\text{-}0.39^{a}$ (10 min)	3.06^{a}	20	
Cu_2O electrodeposited-stainless steel		-1.10	~5	$7.64\text{-}15.29^{a}$ (10 min)	11.9^{a}	38	
$Cu_{88}Sn_6Pb_6$ alloy foil	2M HCl/Two compartments (Nafion 117)	-0.65	0.24	$70.99^{\ a,b}$ (2 h)	$10.6^{a,b}$	34.3	[A.23]
	1.5M HCl-0.5M NaCl/Two compartments (Nafion 117)	-0.70	0.36	$90.93^{\ a,b}$ (2 h)	$13.5^{\ a,b}$	28.2	
	1.5M HCl-0.17M $MgCl_2$/Two compartments (Nafion 117)	-0.70	0.38	$96.77^{\ a,b}$ (2 h)	$14.4^{a,b}$	34.1	
	1.5M HCl-0.17M $CaCl_2$/Two compartments (Nafion 117)	-0.70	0.39	$103.76^{a,b}$ (2 h)	$15.4^{a,b}$	29.6	
	1.5M HCl-0.17M $BaCl_2$/Two compartments (Nafion 117)	-0.70	0.41	$118.59^{\ a,b}$ (2 h)	$17.6^{a,b}$	36.3	
	1.5M HCl-0.08M $AlCl_3$/Two compartments (Nafion 117)	-0.70	0.43	$120.29^{a,b}$ (2 h)	$17.9^{a,b}$	17.8	
	1.5M HCl-0.08 M $NdCl_3$/Two compartments (Nafion 117)	-0.70	0.61	$182.35^{a,b}$ (2 h)	$27.1^{a,b}$	34.6	
	1.5M HCl-0.08 $MLaCl_3$/Two compartments (Nafion 117)	-0.70	0.68	$193.79^{a,b}$ (2 h)	$28.8^{a,b}$	35.7	
	1.5M HCl-0.33 M $ZrCl_4$/Two compartments (Nafion 117)	-0.70	0.45	$142.51^{a,b}$ (2 h)	$21.2^{a,b}$	23.7	
	0.01M CH_3COOH-0.01M CH_3COONa/Two compartments (Nafion 117)	-0.80	0.29	$60.85^{a,b}$ (2 h)	$9.06^{a,b}$	10.2	
	0.01M CH_3COOH-0.003M $BaCl_2$/Two compartments (Nafion 117)	-0.80	0.39	$78.61^{a,b}$ (2 h)	$11.7^{a,b}$	7.9	
	0.01M CH_3COOH-0.0016M $LaCl_3$/Two compartments (Nafion 117)	-0.80	0.96	$175.57^{a,b}$ (2 h)	$26.1^{a,b}$	7.1	
	0.01M CH_3COOH-0.05M $LaCl_3$/Two compartments (Nafion 117)	-0.80	0.98	$186.05^{a,b}$ (2 h)	$27.7^{a,b}$	6.7	
	0.01M CH_3COOH-0.01M CH_3COONa/Two compartments (Nafion 117)	-1.75	5.96	$226.56^{a,b}$ (2 h)	$33.7^{a,b}$	0.5	
	0.01M CH_3COOH-0.0016M $LaCl_3$/Two compartments (Nafion 117)	-1.75	6.26	$248.99^{a,b}$ (2 h)	$37.1^{a,b}$	0.8	
$Cu_{63.9}Au_{36.1}$ on nanoporous Cu films	0.5 M $KHCO_3$/ Two compartments H-type	- 1.00	~0.85	-	-	15.9	[A.24]
Electroplating of Cu on carbon paper	SPE (Nafion)/ Two compartments	-	11.1	-	-	0.54	[A.25]
	SPE (SPEEK)/ Two compartments	-	8.9	-	-	0.44	
Cu foil electropolishing in H_3PO_4	0.1M $KHCO_3$/ Two compartments (AMV Selemion)	-1.40	~10	-	-	~0.13	[A.26]
Cu nanocluster thermally deposited-ZnO (1010)	0.1M $KHCO_3$/ Two compartments (Nafion)	-1.45	~12	9.44^{a} (1 h)	4.25^{a}	2.8	[A.27]
Cu nanocluster (111)		-1.45	~12	3.84 x $10^{-2\ a}$ (1 h)	0.17^{a}	0.1	
Cu_2O electrodeposited on carbon paper	SPE (CMI-7000)/Two compartments MEA	-2^{c}	~3.7	-	-	5	[A.28]
	SPE (AMI-7001)/Two compartments MEA		~2.4	-	-	20	
Cu/CuO nanopowder painted carbon GDE	1M $KHCO_3$/ Two compartments (Nafion 117)	-1.40	17.3	-	-	2.5	[A.29]

Ru/Mo-based electrodes							
Electroplated Ru on Cu foil	0.2M Na_2SO_4/ Two compartments (Na_2SO_4/agar bridge)	-0.54	0.08	-	-	42	[A.30]
Teflon-supported Ru on Cu foil		-0.56	0.09	15.84 (18.6 h)	-	-	
Mo foil on Cu wire	0.2M Na_2SO_4/Undivided	-0.80	0.05	-	-	55	[A.31]
	0.05M H_2SO_4/Undivided	-0.69	0.31	-	-	46	
Mo foil-Cu (KOH/HF pre-treated)	0.2M Na_2SO_4/Undivided	-0.80	0.12	-	-	84	
RuO_2+TiO_2 (35/65)-Ti	0.05M H_2SO_4/Two compartment	-0.55	~5	9.7 (-)	-	24	[A.32]
RuO_2+TiO_2 (20/80)-Ti		-0.55	~5	3.5 (-)	-	5	
RuO_2+MoO_2+TiO_2 (25/30/45)-Ti		-0.55	~5	10.2 (-)	-	12	
RuO_2+Co_3O_4+SnO_2+TiO_2 (20/10/8/62)-Ti		-0.55	~5	6.7 (-)	-	7	
RuO_2+TiO_2 (35/65)-Ti	0.2M Na_2SO_4/Two compartment	-1.48	0.06	8.4 (-)	-	76	
	0.5M $KHCO_3$/Two compartment	-1.50	0.1	1 (-)	-	5	
	Phosphate buffer 0.2M/Two compartment	-1.44	0.08	5 (-)	-	35	
RuO_2 + Co_3O_4 + SnO_2+ RuO_2+ Co_3O_4 + SnO_2 + TiO_2 (20/10/8/62)-Ti	0.2M Na_2SO_4/Two compartment	-1.49	0.05	6.8 (-)	-	53	
TiO_2/RuO_2 (75/25)-Cu (deposited 300 mC/cm^2)	0.5M $KHCO_3$/ Undivided-Rotating-disk electrode assembly	-1.00	5	-	-	29.8	[A.33]
RuOx thermally deposited-Ti	0.5M $KHCO_3$/Undivided-Three electrodes	-0.80	~2	~1.60-2.99^a (2-8 h)	~0.35-0.16^a	30.5-17.2	[A.34]
RuOx/Cu thermally deposited-Ti		-0.80	~2	~1.39-3.95^a (2-8 h)	~0.30-0.21^a	18.2-41.3	
RuOx/Cd thermally deposited-Ti		-0.80	~2	~1.17-4.27^a (2-8 h)	~0.26-0.23^a	20.4-38.2	
RuO_2-painted (5-6 layers)-BDD	0.4M Britton–Robinson sol. (H_3BO_3+H_3PO_4+$C_2H_4O_2$)/ Two compartments	-0.80	~5	31.31 (~6 h)	3.44^a	8.12	[A.35]
RuOx sprayed-Pt	0.5M $NaHCO_3$/ Two compartments H-type cell (Nafion 117)	-0.80	~1.2	-	-	30.5	[A.36]
RuO_2/TiO_2 nanoparticles-Pt		-0.80	~1.2	-	-	40.2	
RuO_2/TiO_2 nanotubes-Pt		-0.80	~1.2	-	-	60.5	
MoS_2-rods in TiO_2 nanotubes	0.1M $KHCO_3$/Undivided, three electrodes	-1.30	~0.75	202.24^a (6 h)	-	44.9	[A.37]
Other transition metal: Fe, Ti and Hg							
Everitt's salt (ES, $K_2Fe''[Fe''(CN)_6]$) coated-Pt	1,2-dihydroxybenzene-3,5-disulfonate (tiron) ferrate(III) complex-C_2H_6O/Three compartment (glass frit)	-1.00	-	0.32^a (6 h)	3.86 x 10$^{-2\ a}$	-	[A.38]
Everitt's salt coated-Pt	$[Fe(C_6H_2(OH)_2(SO_3)_2)_2]$-$CH_3OH$/ Two compartment (glass frit)	-0.90	-	5.15^a (5 h)	-	14.5	[A.39]
	$[Fe(C_6H_2(OH)_2(SO_3)_2)_2]$-$C_2H_6O$/ Two compartment (glass frit)	-1.10	-	0.04^a (5 h)	-	0.06	
	$Na_3[Fe(CN)_5(H_2O)]$-CH_3OH/ Two compartment (glass frit)	-0.90	-	4.74^a (5 h)	-	15.5	
	$[NH_4]_2[CrCl_5(H_2O)]$-C_2H_6O/ Two compartment (glass frit)	-1.10	-	0.04^a (5 h)	-	0.05	
	$K[Cr(C_2O_4)_2(H_2O)_2)]$-CH_3OH/ Two compartment (glass frit)	-0.90	-	5.09^a (5 h)	-	14.5	
	$K[Cr(C_2O_4)_2(H_2O)_2)]$-C_2H_6O/ Two compartment (glass frit)	-1.10	-	0.03^a (5 h)	-	0.04	
Everitt's salt supported-Pt	0.1M KCl-10mM $Na_3[Fe(CN)_5(H_2O)]$)-15 mM CH_3OH/ Two compartment (glass frit)	-0.70	-	2.62-7.20^a (2-9 h)	1.20-0.69^a	56.3-45.3	[A.40]
Indigo ($C_{16}H_{10}N_2O_2$)/ graphite-Pt		-0.70	-	1.60-4.35^a (2-9 h)	0.69-0.42^a	70.2-37.2	
Alizarin ($C_{14}H_8O_4$)/ graphite-Pt		-0.50 to -0.70	-	2.18-2.50^a (3 h)	0.63-0.72^a	44.3-69.4	
ES supported- Fe		-0.30 to -0.70	-	5.47-5.66^a (5 h)	0.95-0.98^a	45.5-45.7	
Indigo/ graphite-Fe		-0.70	-	6.24^a (5 h)	1.08^a	42.8	
2-aminoanthraquinone/ graphite-Fe		-0.70	-	3.42^a (5 h)	0.59^a	31	
Alizarin ($C_{14}H_8O_4$)/ graphite/Fe		-0.70	-	3.55^a (5 h)	0.62^a	30.8	

p-benzoquinone/graphite powder supp. on Fe		-0.70	-	4.48[a] (5 h)	0.78[a]	36	
Fe(II) TPP (tetraphenylporphyrin) evaporated-Pt	2-hydroxil-1-nitrosonaphthalene-3,6-disulphonatocobal(II) l in 0.1M KCl-CH_3OH/ Undivided three electrodes (proton exchange membrane)	-0.50	0.36	3.04[a] (5 h)	0.35[a]	12.2	[A.41]
Co(II) TPP evaporated-Pt		-0.50	0.39	4.35[a] (5 h)	0.50[a]	15.1	
Ni(II) TPP evaporated-Pt		-0.50	0.15	3.17[a] (5 h)	0.37[a]	14.4	
Cr(III) TPPCl supported-Pt		-0.50	0.10	1.67[a] (5 h)	0.19[a]	11.6	
Fe(III) TPPCl supported-Pt		-0.50	0.37	6.14[a] (5 h)	0.71[a]	11.1	
Co(II) TPP supported-Pt plate	Aquopentacyanoferrate (II) ($Na_3[Fe(CN)_5(H_2O)$-0.1M KCl-CH_3OH/ Undivided, three electrodes (proton exchange membrane)	-0.50	0.07	3.33[a] (5 h)	0.35[a]	32.9	
Fe-S/Pan/PB electrochemical laminated-Pt (PB: Prussian blue; PAn: polyaniline)	0.5M KCl/Two compartments H-type	-0.80	-	0.04[a] (24 h)	5.62-6.28 x 10^{-4} [a]	6.8	[A.42]
Fe-T/Pan/PB-Pt			-	0.07[a] (24 h)	1.03-1.15 x 10^{-3} [a]	8.3	
Fe-C/Pan/PB-Pt			-	0.11[a] (24 h)	1.64-1.83 x 10^{-3} [a]	12.2	
Fe-C/Pan/PB-Pt-self assembled	0.2M KCl/ Two compartments H-type		-	0.28[a] (24 h)	4.08-4.55 x 10^{-3} [a]	10.1	
			-	0.05[a] (24 h)	7.03-7.85 x 10^{-4} [a]	5.2	
	0.5M KCl/ Two compartments H-type		-	0.04 [a] (24 h)	5.62-6.28 x 10^{-4} [a]	6.3	
Post-transition Ga- based electrodes							
n-GaAs-crystal-(111)As	0.2M Na_2SO_4/ Two compartments (Na_2SO_4/agar bridge)	-1.20 to -1.40	0.16-0.2	-	-	100	[A.43]
n-GaAs-crystal-(111)Ga			0.34	-	-	30-80	
n-GaAs-crystal-(110)Ga			0.13	-	-	14	
n-GaAs-crystal-(100)Ga			0.15-0.16	-	-	1-0	
Pt metal group metal- based electrodes							
Pd with Cu electrodeposited (coverage of 10)	0.1M $KHCO_3$/-	-1.60	-	-	-	2.28	[A.44]
Pd-H with Cu electrodeposited (coverage of 10)		-1.60	-	-	-	6.97	
Pd disk (HNO_3/NaOH treated)	0.5M $NaClO_4$+10mM Pyridine/ Two compartment (glass frit)	-	0.04	-	-	30	[A.45]
Pt/C powder deposited-carbon paper	SPE (Nafion 117)/Two compartments MEA flow cell	-0.35	-	-	-	40	[A.46]
Pt/C powder deposited-carbon paper	SPE (Nafion 117)/Two compartments MEA flow cell	-0.40	~20	0.40[a] (1 h)	~7.44[a]	35	[A.47]
Pt-Ru/C powder deposited-carbon paper		-0.45	~15	10[a] (1 h)	~186[a]	75	

[a] Calculated from reported data

[b] Data for total CO_2 reduction to various products (including CH_3OH)

[c] Reference electrode not provided

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