Electrochemical membrane reactors for the utilisation of carbon dioxide

Ivan Merino-Garcia[a,], Enrique Alvarez-Guerra[a], Jonathan Albo[b], Angel Irabien[a*]

[a]*Department of Chemical and Biomolecular Engineering, University of Cantabria, Avenida de los Castros s/n, 39005 Santander, Cantabria, Spain.*

[b]*Department of Chemical Engineering, University of the Basque Country, Apdo. 644, 48080, Bilbao, Spain.*

[*]Corresponding author; e-mail: angel.irabien@unican.es

Climate Change is among the greatest challenges for humankind in the 21st century. Carbon Capture and Utilisation (CCU) allows the production of value-added chemicals from CO_2, reducing at the same time the undesirable effects of global warming.

Among the available methods for CO_2 utilisation, the electrochemical reduction appears as a promising technological solution to store intermittent renewable energy in the form of chemical bonds, leading to valuable chemicals such as formic acid, methanol or ethane, which can be put back into the market.

The application of electrochemical membrane reactors (ecMRs) for the valorisation of CO_2 allows the separation of the catholyte and anolyte compartments, leading to an enhanced separation of reaction products and avoiding their re-oxidation. Among these membrane-based reactors, the utilisation of Membrane Electrode Assemblies (MEAs), where the cathode and anode are coupled with a conductive membrane, are gaining importance. Besides, Gas Diffusion Electrodes (GDEs) are able to reduce mass transfer limitations and therefore, enhanced efficiencies in the process of CO_2 electroreduction.

Accordingly, the aim of the present review is to compile the literature on the application of membrane reactors for CO_2 electroreduction, paying special attention to the type of membrane, reactor configuration and catalytic material in the electrochemical reactor.

Then, a performance comparison in terms of Faradaic efficiency and products reported up to date, is carried out.

1. Introduction

Climate change is one of the most significant challenges to achieving sustainable development. The emissions of carbon dioxide (CO_2) to the atmosphere need therefore to be drastically reduced in order to alleviate the proven effects of global warming [1, 2].

Among the available CO_2 mitigation strategies, Carbon Capture and Utilisation (CCU) to produce useful chemicals from CO_2 [3-5] is particularly interesting, since it may alleviate our rely on fossil fuels for energy and chemical synthesis [6], promoting, at the same time, new technical sinks in the carbon life cycle.

There are different techniques to activate and convert CO_2 at low temperatures. Among them, photoreduction (photocatalysis), electrochemical reduction (electrocatalysis) and reforming of CO_2 are considered the most interesting ones [7].

The technology for CO_2 photoreduction is still incipient. Photocatalytic materials seem to be unstable and current efficiencies are still low. Besides, plasma methods are clean and fast, but their energy efficiency is still very low (around 6 %). On the other hand, conventional methods (i.e. reforming) involve high cost associated to the needs of high thermal power [7].

In contrast, the electrocatalytic reduction of CO_2 is an attractive solution since it allows obtaining hydrocarbons and oxygenates with a simple procedure at low operation temperatures. In addition, this technique shows promise to reduce greenhouse gas

emissions and control the anthropogenic carbon cycle by transforming CO_2 to fuels and chemicals [8]. Due to the environmental and potential economic benefits, different systems have been developed for the electrochemical conversion of CO_2 [9].

The efficiency of this process can be enhanced by selecting a highly active electrocatalytic material, increasing the pressure of CO_2 (using gas diffusion electrodes (GDEs)) or applying efficient electrochemical reactor configurations, among others [10].

Besides, the application of membranes in electrochemical reactors for CO_2 reduction is also interesting, since it allows separating the cathodic and anodic reactions that occur simultaneously in a redox system. Thus, studies on CO_2 conversion in divided electrochemical membrane reactors (ecMRs) are commonly found in literature [11].

Membranes may play a very important role, since they allow the use of different catholyte and anolyte volumes, enhancing the separation of products, leading to technical advantages in the reduction process. Besides, Membrane Electrode Assemblies (MEAs), where cathode and anode are coupled with conductive membrane materials, are also an interesting approach. The literature shows the application of different ion exchange membranes for the electrochemical reduction of CO_2 in divided cells, namely cation exchange membranes (CEMs), usually Nafion®, and anion exchange membranes (AEMs) such as Selemion™. In addition, the phase involved in these reactors has also been taken into account. Works based on gas phase at the cathode side are emerging due to the low solubility of CO_2 in water [12], with the aim to improve mass transfer limitations occurring in liquid phase systems. Moreover, the utilisation of gas phase in both, the cathode and anode compartments, has been reported in a few works [13, 14], although the efficiencies of those systems are still low, and therefore, further developments are needed.

There are several reviews on different aspects related to CO_2 electrochemical conversion [6, 9, 15-17]. However, none of them pays specific interest to the discussion on membrane reactor configurations for CO_2 electroreduction. Thus, the aim of the present review is to discuss the different reports on electrochemical membrane reactor configurations for CO_2 utilisation. A discussion of relevant studies on the topic are presented, emphasizing on: membrane materials, electrochemical reactor designs and catalytic material for each system.

2. Electrocatalytic reaction analysis

The performance of a CO_2 electrochemical reduction process is in general evaluated in terms of *Faradaic efficiency* (*FE*), *energy efficiency (EE)* and *current density (CD)*. The *FE* represents the percentage of electrons that end up in the desired product:

$$FE\ (\%) = \frac{z \cdot n \cdot F}{Q}\ x100 \qquad (1)$$

where *z* is the number of exchanged electrons, *n* is the number of moles for a product, *F* is the Faraday constant (96,485 $C \cdot mol^{-1}$), and *Q* represents the charge passed in the system (C).

Besides, the *energy efficiency* (*EE*) refers to the amount of energy in the products divided by the amount of electrical energy put into the system [8], as defined by equation 2:

$$EE = \sum_k \frac{E_k^0 \cdot FE_k}{E_k^0 + \eta}\ (dimensionless) \qquad (2)$$

where E^0_k is the equilibrium cell potential for a specific product k (V), FE_k is the *FE* of product k, and η is the cell overpotential (V) [6].

And finally, the *current density* (*CD*), which is related to the conversion rate of the electrochemical reaction, usually expressed in $mA \cdot cm^{-2}$.

The goal for an efficient CO_2 electroreduction process is to achieve high *EEs* and reaction rates for CO_2 conversion (i.e., high *CD*). Therefore, high *FE* and low overpotentials on the cathode and anode are necessary in order to bring the technology closer to an industrial scale.

Moreover, the reduction products obtained from the electroreduction of CO_2 are diverse, mainly including carbon monoxide (CO), formic acid (HCOOH), formaldehyde (CH_2O), methanol (CH_3OH), methane (CH_4), ethylene (C_2H_4) or ethanol (CH_3CH_2OH), depending on the number of electrons involved as shown from equation 3 to equation 9. It is also very common to find a mixture of products [6, 16, 18].

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (3)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \quad (4)$$

$$CO_2 + H^+ + 2e^- \rightarrow HCOO^- \quad (5)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \quad (6)$$

$$CO_2 + 6H^+ + 6e \rightarrow CH_3OH + H_2O \quad (7)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (8)$$

$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4\,H_2O \quad (9)$$

The mechanisms for CO_2 reduction on metallic electrodes have been hypothesized by several authors, as summarized in Figure 1 [6, 8, 16].

In general, metal groups 1 and 2, which lead to CO and HCOOH formation, are widely found in the literature [19, 20]. On the other hand, studies applying metals included in the group 3 for alcohols and hydrocarbon formation are less abundant [21, 22].

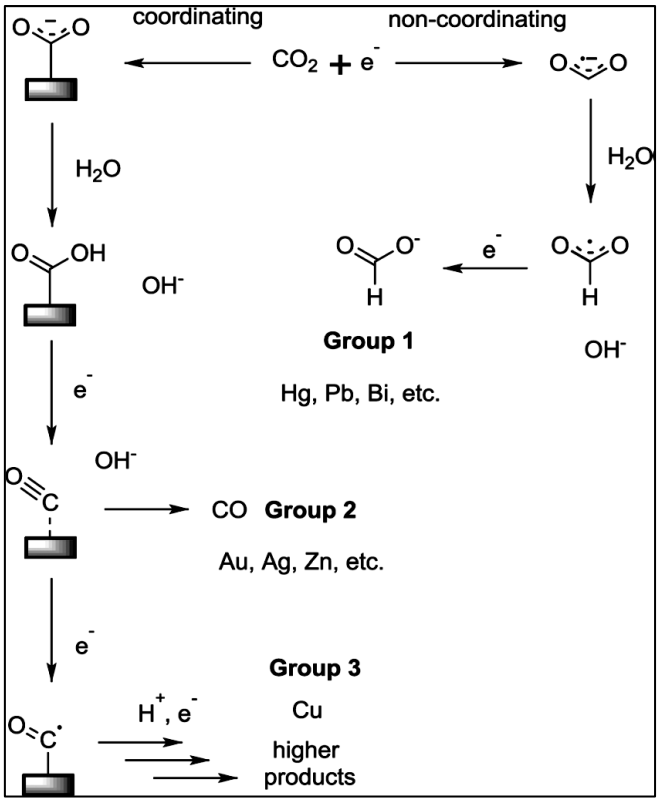


Figure 1. Mechanisms for the electrochemical reduction of CO_2 in water at metal surfaces. Reproduced with permission from ref. [8].

In order to give an overview of the available literature in the valorisation of CO_2 using ecMRs, Figure 2 shows the products distribution of reported systems.

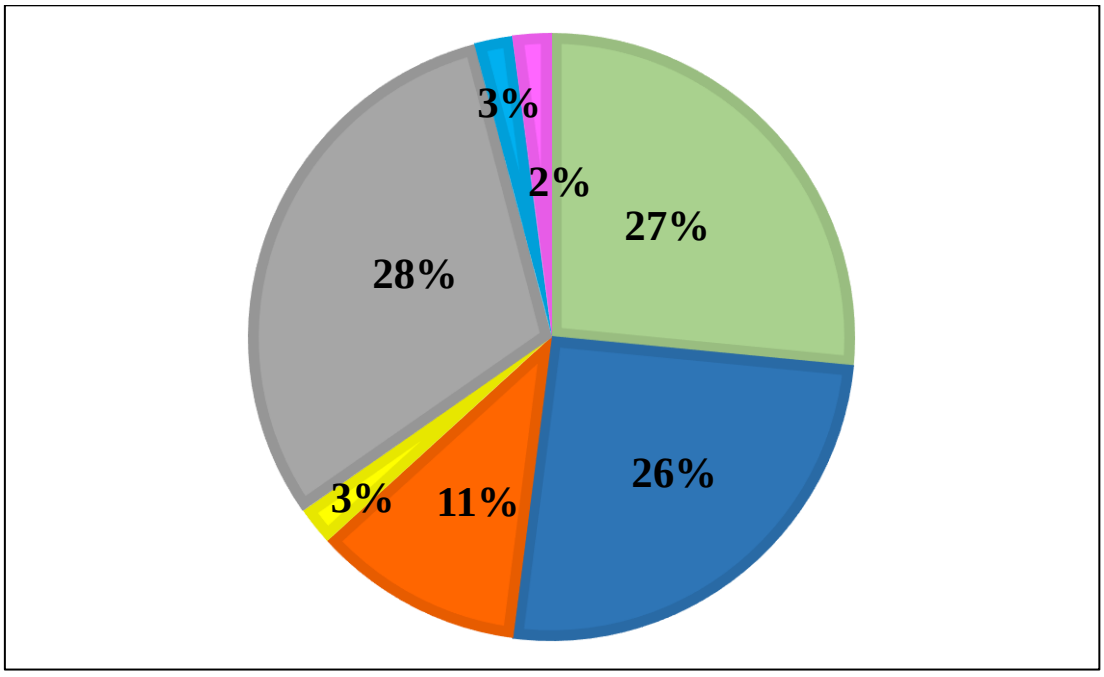


Figure 2. Distribution products, sreports for CO_2 utilisation in ecMRs. Notation: HCOOH; CO; CH_4; C_2H_4; C_2H_6; CH_3OH; dimethyl carbonate (DMC) [revised March 2016].

HCOOH and CO are the main products in ecMRs, due to their lower number of electrons and protons exchanged. Besides, the production of hydrocarbons (i.e. CH_4, C_2H_4 and C_2H_6) are gaining increasing importance, in spite of the higher number of electrons and protons required in the process [9, 15]. On the other hand, CH_3OH (3 %) and DMC (2 %) have been scarcely found to be the main products in ecMR systems. Considering the relevance of the cathode material in the CO_2 electroreduction process, Figure 3 shows the type of catalysts applied for the production of different products in ecMR systems.

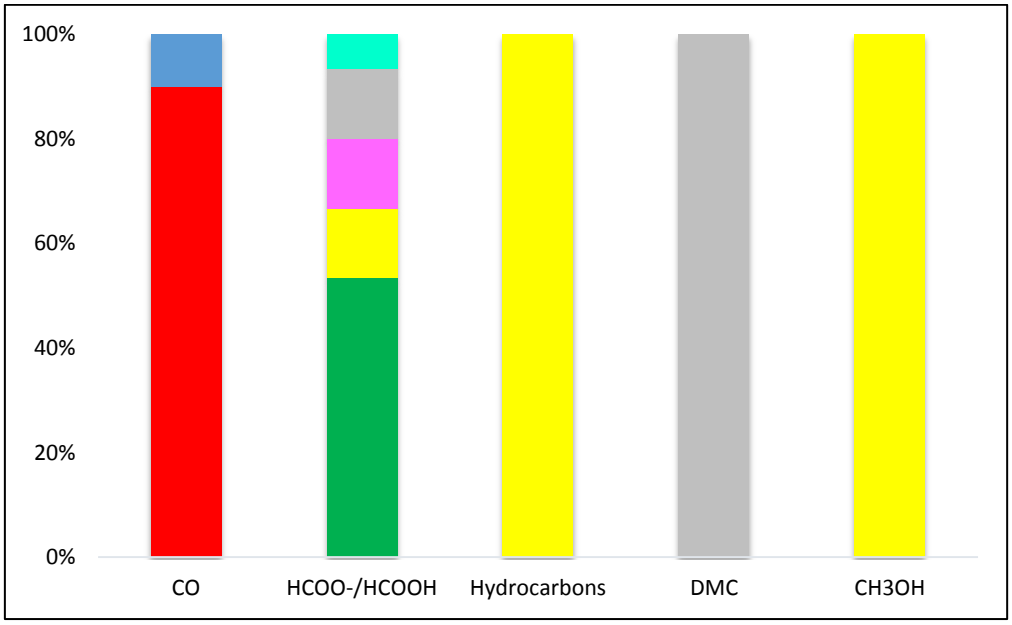


Figure 3. Different catalysts applied for the formation of different products obtained. Notation: Ag; Ni; Sn; Pb; Pt; Cu; Cu-Sn

As observed, CO is generally obtained in ecMRs with Ag-based catalysts (90 %). Besides, Sn-based catalysts are the most common reported materials for HCOOH

production, although Pb, Pt, and Cu-based catalysts can be also active for HCOOH formation in ecMRs [20, 23-25]. Cu-based catalyst have been mainly used for the electrochemical conversion of CO_2 to hydrocarbons and CH_3OH [21, 26]. DMC has been obtained at Pt-Nb catalysts (95 % Pt). The figure, thus, demonstrates the importance of the cathodic material selection in the valorisation of CO_2, in order to achieve high efficiencies for different products.

Some electrocatalysts for the electrochemical reduction of CO_2 gave desirable product selectivity under continuous operation, but only a few of them have resulted in high efficiency production (e.g. Sn and Pb to obtain HCOOH). In this way, the selectivity to the desired product with high efficiencies strongly depends on other aspects related to the process such as the composition of electrocatalysts, the catalytic mechanism for CO_2 reduction or operation conditions (pH, electrolyte, potential, temperature, pressure, etc.) [18].

3. Electrocatalytic membrane reactors

The main limitations of CO_2 valorisation processes are related to the slow kinetics of CO_2 electroreduction, high-energy consumption and low *EE* of the process. To tackle those issues, different reactor configurations have been developed, in order to enhance process performance and bring the technology for CO_2 electroreduction closer to the industrial-scale [18].

This section analyses the different electrochemical reactor reported in literature, paying special attention to the relative position of the electrodes and the membrane in each configuration. The different reactor configurations applied along the time are presented in Figures 4 to Figure 7.

Firstly, undivided electrochemical reactors, in which dense plates-type electrodes are separated by a liquid phase that acts as both anolyte and catholyte (Figure 4.a) were conventionally applied. In these cells, product recuperation is not simple and requires an additional separation step, increasing process costs.

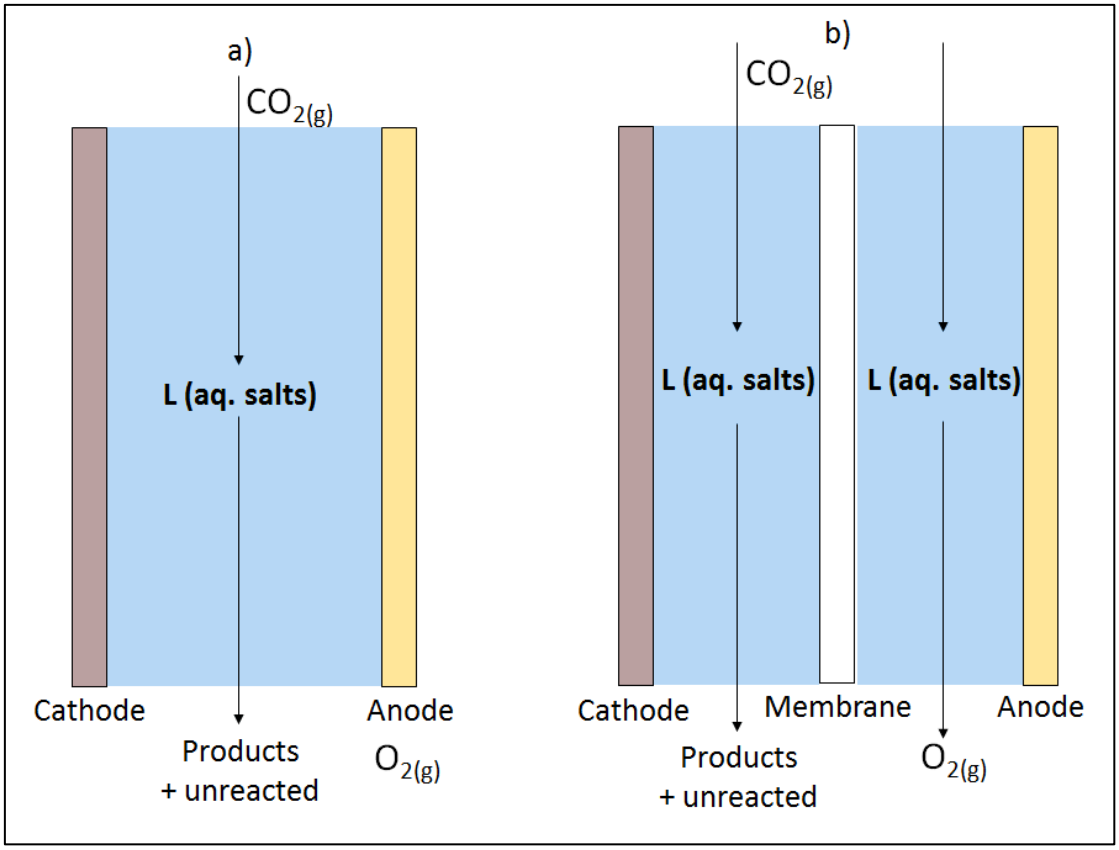


Figure 4. Conventional undivided electrochemical reactor (a) and electrochemical reactor separated by an ion exchange membrane (b).

Besides, Figure 4.b. shows an ecMR with two compartments divided by an ion exchange membrane. In this case, the membrane isolates cathodic and anodic reactions, which may occur simultaneously in an electrochemical process, leading to an enhanced separation of products and the avoidance of re-oxidation reactions [11]. Different research groups have applied plate electrodes in two-compartment cells separated with an ion exchange membrane [19, 23, 24, 26-36]. In general, the application of CEMs, where the transport of protons is favoured, is preferred [20, 23, 24, 26, 28-36] with

respect to the use of AEMs [19, 27], where species such as bicarbonate are mainly transported through the membrane.

The type of membrane [11], together with the selection of the electrolyte (e.g. H^+ or K^+ can cross the membrane in H_2O or KOH aqueous anolytes, respectively), is very important in the process. When a CEM is applied to the CO_2 electrochemical reduction process, the following reactions are observed [11]:

$$CO_2 + 2\,H^+ + 2\,e^- \rightarrow CO + H_2O \qquad (10)$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad (11)$$

However, with AEMs the anionic species travel from the cathode to the anode (e.g. HCO_3^- from an aqueous solution of $KHCO_3$ as catholyte). In this case, CO_2 evolved at the anode side and needs to be further separated from the O_2 generated in the anode. The typical reactions for the CO_2 electroreduction to CO using AEMs at the cathode side are as follows [11]:

$$3\,CO_2 + H_2O + 2\,e^- \rightarrow CO + 2\,HCO_3^- \qquad (12)$$

$$2\,CO_2 + 2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,HCO_3^- \qquad (13)$$

The main aspects that limit these electrochemical reactions are mass transport across the membrane, the nature of the reaction medium and the required protons of the product of interest. The procedure to activate the membranes prior their use is also a key factor to achieve an enhanced CO_2 electrochemical reduction [37].

Besides, polarization losses in the electroreduction of CO_2 are usually related to the transport of species and concentration gradients, which may basically depend on the membrane. The effect of using a CEMs or AEMs on polarization losses was recently studied by Singh et al. [38], concluding that losses when using a CEM are higher than

those for an AEM or without membrane. In spite of that, most of the works on CO_2 electrochemical reduction are performed with Nafion® CEMs. Other variables such as cathode and anode overpotentials, mass transfer, pH between cathode and anode and other operation conditions (e.g. CO_2 flow and pressure, *CD*, etc) should be also taken into account in order to reduce polarization losses. In general, CO_2 reduction to CO involves a high level of polarization. However, this level decreases as the number of required electrons to produce a specific product increases. Besides, different ways to minimize polarization losses, achieving high *CDs* to favour CO_2 reduction vs. hydrogen evolution reaction (HER) have been proposed [38]. It seems that the electrolyte should be close to neutral pH.

Moreover, in order to overcome mass transfer limitations occurring in ecMRs, GDEs, in which the catalytic material is dispersed by different methods onto a porous structure, have been used for the electrochemical valorisation of CO_2 [10, 21, 25, 39-44]. The development of suitable supports to achieve a good catalyst dispersion and transport of reactants (i.e. CO_2) is essential for an enhanced efficiency of the process. Porous carbon papers have been usually applied for the fabrication of GDEs [39], although different polymers, which enhanced properties, are currently under development [45].

Depending on the relative position of the GDE with respect to the ion exchange membrane, different reactor configurations are reported (Figure 5). Particularly, Figure 5a shows a catalytic layer–membrane configuration [46]. Additionally, MEAs, where cathode-membrane-anode are coupled and thus, the contact and transport of species between the electrodes are enhanced, can be found in literature [11, 47-49].

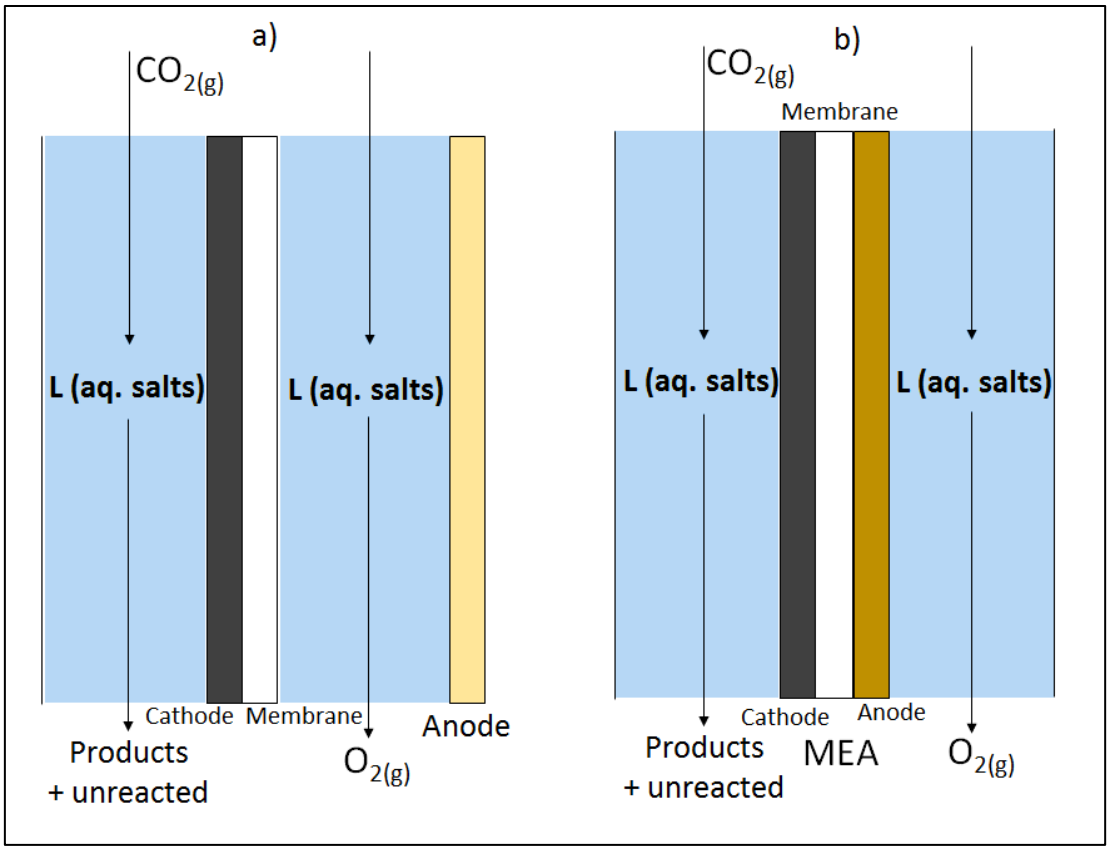


Figure 5. Catalysts dispersed at the cathode coupled with an ion exchange membrane (a) and, both electrodes coupled with the membrane (MEA) (b).

Furthermore, due to the low solubility of CO_2 in water and the possibility to avoid HER, the conversion of CO_2 directly in gas phase has aroused great interest recently [11, 22, 50-57]. In this configuration, CO_2 transport resistances in the catholyte may be suppressed. Figure 6 shows different reactor configuration approaches using CO_2 gas at the cathode.

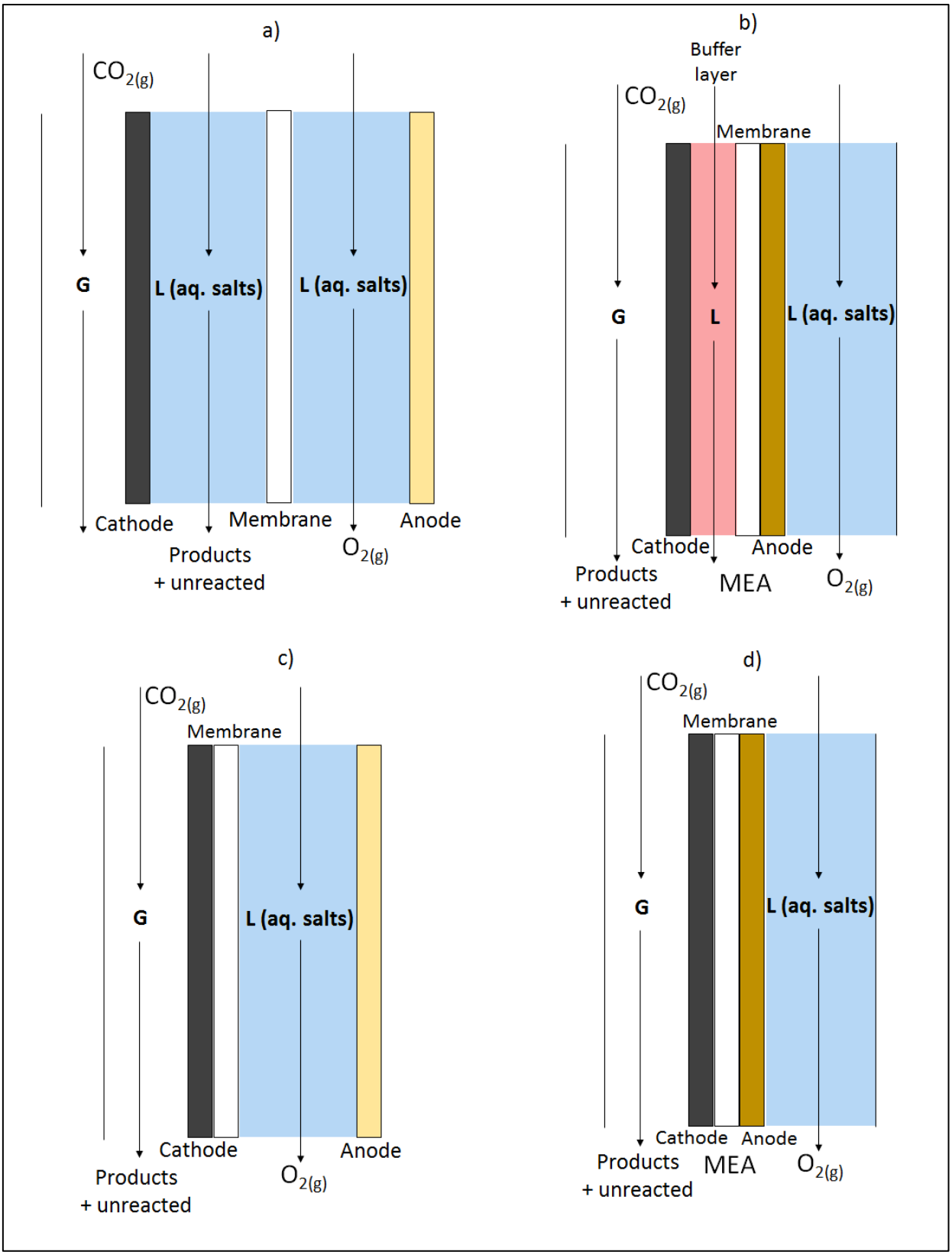


Figure 6. Different electrochemical reactor configurations for CO_2 valorisation in gas phase: gas phase at the cathode separated to the catholyte (a), gas phase at the cathode

with a liquid buffer layer (b), cathode coupled to a membrane without buffer layer (c), and MEA configuration (d).

The simplest configuration is shown in Figure 6.a, where a GDE is placed between the gas stream and the catholyte, separating both phases. An alternative, is the replacement of the catholyte by a pH-buffer layer (aqueous salt solution), usually applied between the cathode and the membrane (Figure 6.b). This configuration permits the transport of ionic species (i.e. H^+) by using different aqueous salts such as $KHCO_3$ [11, 50]. For instance, a large increase in the selectivity for CO evolution (efficiency of 82 %) using Ag-based catalyst as working electrode was observed with respect to a configuration in which the buffer layer was not included [11]. Wu et al. [50] discussed that the inclusion of a pH-buffer layer (0.1 M $KHCO_3$) allowed to dominate CO_2 reduction to $HCOO^-$ (*FE* around 90 %) over HER using a sprayed Sn ink onto a GDL as cathode.

Figure 6.c and Figure 6.d present the cell configuration for the reduction of CO_2 in gas phase. In the first case (Figure 6.c); the MEA contains a porous cathode coupled with the membrane, with the anolyte solution between the anode and membrane [51-53]. In the second configuration (Figure 6.d), the electrodes are sandwiched together with the membrane (MEA) [11, 22, 54-57] facilitating the transport of ionic species, which may be beneficial for an effective valorisation of CO_2 into more reduced products such as CH_4 and C_2H_4 [17].

Finally, the development of electroreduction processes completely in gas phase at both electrode compartments is under development. This configuration may overcome mass transfer limitations and facilitate the separation of products. The available literature in this regard is still scarce and it seems that further developments are required [13, 14]. Cook et al. [13] firstly developed gas-gas ecMRs for CO_2 reduction using a Nafion® 117 membrane. They observed the formation of CH_4, C_2H_4 and C_2H_6 as major products.

Besides, Figure 7 shows the scheme of the electrocatalytic cell applied by Kriescher et al. [14] for CO_2 reduction to hydrocarbons.

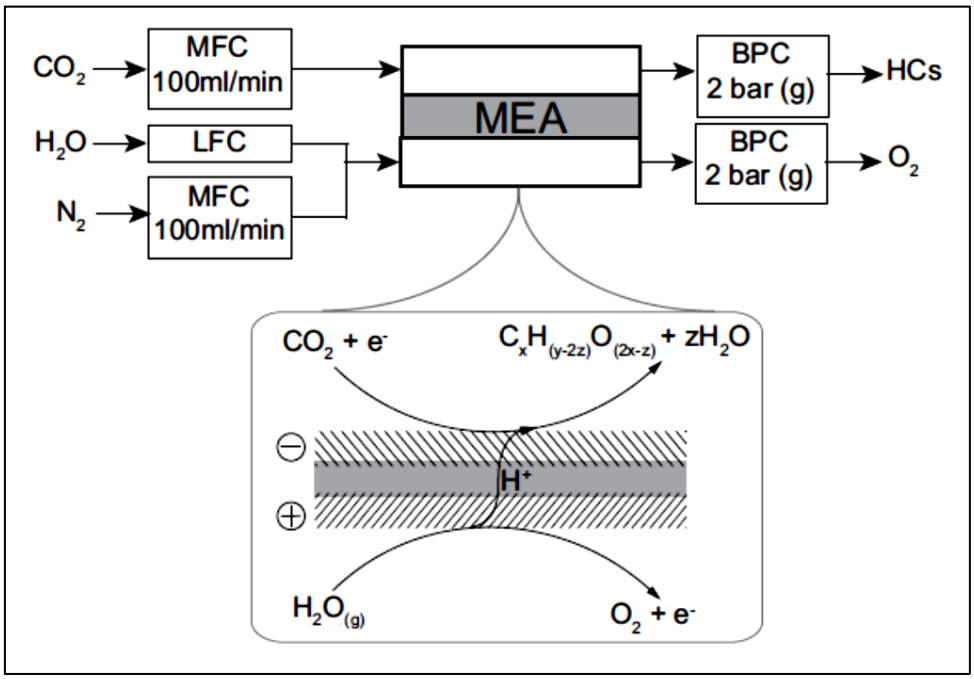


Figure 7. Gas-gas ecMR used by Kriescher et al. [55]. Reproduced with permission from ref. [14].

The effect of temperature in the electroreduction of CO_2 to hydrocarbons was analysed when CO_2 and N_2 were supplied to the cathode and anode compartments, respectively. The applied MEA consisted on a Fumatech®, Fumapem F-14001 CEM, a Cu-electrocatalyst (working electrode) and Ti covered with Ir as anode. The concentration of the desired product and current efficiencies were still very low (*FE* to CH_4= 0.12 % at 6 V and 70 ºC). They finally suggest that a higher CO_2 residence time, the development of new membrane materials with high proton conductivity and low water transmission rates, and optimization of the three-phase interface (electrode, proton conductor and catalyst) may lead to an enhanced electroreduction of CO_2 in gas phase. In any case, further efforts in highly active catalysts, durability of the electrodes and new reactor configurations should be tackled in order to apply this technology for

technical applications. Finally, it is important to take into account the manufacture costs associated to the fabrication of electrochemical reactors, which is not generally discuss in the literature.

4. Main results for CO_2 utilisation in ecMRs

The section is divided in the two main electrochemical reactors: (i) Liquid-Liquid (L-L) ecMRs (even though gas phase may be also present in the cathode side) and (ii) Gas-Liquid (G-L) ecMRs (where gas phase is only in the cathode). Then the subsections are divided by the nature of the membranes and the applied catalysts, in order to give an overview of reported studies in terms of *FE*, *CD* and the voltage (*E)* required in each process with similar catalyst-based materials and membranes.

4.1. Liquid-Liquid (L-L) ecMRs

Table 1 summarizes the type of membranes applied, catalytic materials and experimental conditions in L-L ecMRs for the electrochemical reduction of CO_2. Most of the reported studies employed proton conductive membranes (mainly Nafion®) to separate catholyte and the anolyte, which usually consist of aqueous solutions of $KHCO_3$ and KOH, respectively [10, 11, 20, 21 23, 24, 26, 28-35, 40-43, 46, 47, 49, 58-67] in comparison to those reports where cathode and anode chambers are separated by an AEM [19, 27, 36, 54, 68, 69].

As it can be seen, CO, HCOOH, CH_4 and C_2H_4 are the most common products in L-L ecMRs. Besides Ag, Sn or Pb, and Cu-based electrodes are the common catalysts applied, since they allow to obtain CO, HCOOH and hydrocarbons, respectively, with high *FEs*.

The following subsections critically discuss the reported L-L ecMRs reactors according to the type of membranes and catalysts applied in the CO_2 electroreduction process.

Table 1. Experimental conditions, catalytic materials, main products and significant results for CO_2 valorisation in L-L ecMRs.

Membrane	**Cathode**	**Anode**	**Catholyte**	**Anolyte**	**Products**	**V vs. Ag/AgCl / CD ($mAcm^{-2}$)**	**Main results**	**P (atm) / T (^oC)**	**Ref.**
Nafion®	Sn-GDE	Pt plate	CO_2 , $KHCO_3$	aq. $KHCO_3$	HCOOH, H_2, CO, CH_4	50 mA/cm^{-2}	FE HCOOH= 93 %	1 / 25	[10]
Nafion®	Ag	Pt-Ir (1:1) alloy	CO_2 , $KHCO_3$	aq. KOH	CO, H_2	-1.38 V	FE CO= 40 %	1 / 25	[11]
Selemion™ (AEM)	Ag foil	Pt foil	CO_2 , $KHCO_3$	aq. $KHCO_3$	CO, H_2, HCOOH, CH_4, CH_3OH, C_2H_5OH	-1.6 to -1.3 V	FE CO= 90 %; HCOOH= 8 %	1 / 25	[19]
Nafion® 117	Pb plate	DSA	CO_2 , KCl + $KHCO_3$	aq. KOH	HCOOH	2.5 $mAcm^{-2}$	FE HCOOH= 94.7 % (14.4 mg/L)	1 / 25	[20]
Nafion®117	Cu_2O	Platinized titanium	CO_2 , $KHCO_3$	aq. $KHCO_3$	CH_3OH	-1.3 V	FE CH_3OH= 45.7 %	1 / 25	[21]
Nafion® 450	Mesh tinned-Cu plate	Platinized titanium plate	CO_2 y N2, $KHCO_3$	aq. KOH	HCOOH, H_2, CO, CH_4	22 $mAcm^{-2}$	FE HCOOH= 86%	1 / 25	[23]
Nafion® 117	Sn plate	DSA	CO_2 , KCl + $KHCO_3$	aq. KOH	HCOOH	12.25 $mAcm^{-2}$	FE HCOOH= 70 %	1 / 25	[24]
Polymer electrolyte membrane	Pt-Glassy carbon electrode	Pt wire	Deionized water or $KHCO_3$	Pure deionized water	HCOOH	-	HCOOH: continuous mode (0-35 mM); discontinuous mode (0-18 mM)	1 / 25	[25]
Nafion® 117	Cu foil	Pt foil	CO_2, LiOH in CH_3OH	KOH in CH_3OH	CH_4, C_2H_4, CO, HCOOH	-4 V	FE (CH_4 + C_2H_4)= 78 %	- / -30	[26]
Selemion™ (AEM)	Cu foil	Pt foil	CO_2 , $KHCO_3$	aq. $KHCO_3$	16 different products	-1.35 to -1.07 V	FE CH_4= 40 %; C_2H_4= 25 %; HCOOH= 23 %	-	[27]
Nafion® 112	Cu_2O films	Pt mesh	CO_2 , $KHCO_3$	aq. $KHCO_3$	C_2H_6, C_2H_4, CH_4, CO	-1.3 V	FE C_2H_4= 20 %; CH_4= 5 %; CO= 4 %; C_2H_6= 2.5 %	1 / 25	[28]
Nafion® 117 or no membrane	Cu plate	Pt plate	CO_2 , NaOH or KOH in CH_3OH	NaOH or KOH in CH_3OH	CH_4, H_2	-	Without membrane and using KOH: FE CH_4= 35.6 %	1.2 / 25	[29]
Nafion® 117	Pt/Nb plate	Pt/Nb	CO_2 , CH_3OH	CH_3OH +	DMC	-	DMC: 11.37 mM	-	[30]

	(95% Pt)	plate (95% Pt)	+ [bmim][Br] + CH_3OK	[bmim][Br] + CH_3OK					
CEM	Modified Cu electrodes	Pt mesh	CO_2 , $KHCO_3$	aq. $KHCO_3$	CH_4, C_2H_4, C_2H_6, H_2, CO	-1.9 V	FE C_2H_4= 33 %; CH_4= 10 %	1 / 25	[31]
CEM	Cu mesh	Pt mesh	CO_2 , $KHCO_3$	aq. $KHCO_3$	CH_4, C_2H_4, C_2H_6, H_2, CO	-1.9 V	FE CH_4= 15 %; C_2H_4= 8 %	1 / 25	[32]
Nafion® 117	Cu foil	Pt foil	CO_2, sodium salts in CH_3OH	KOH in CH_3OH	CH_4, C_2H_4, HCOOH, CO, H_2	-3 V	FE CH_4= 70.5 % in $NaClO_4/CH_3OH$	- / -30	[33]
Nafion® 117	Cu wire	Pt plate	CO_2, $LiClO_4$ in CH_3OH	aq. H_2SO_4	CH_4, C_2H_4, CO, HCOOH, CH_3COOH	*-3 V	20 bar: FE CH_4= 25.5 %; CO= 15.1 %; HCOOH= 22.1 %; CH_3COOH= 40.2 %	1-60 / -	[34]
Selemion™ (CEM)	Cu-halide electrodes	Pt plate	CO_2, potassium halides	aq. potassium halides	CH_4, C_2H_4, C_2H_6, CO, C_2H_5OH, H_2	-2.4 V	CuBr electrode and KBr electrolyte: FE C_2H_4= 79.5 %; CH_4= 5.8 %	-	[35]
FAB (AEM) or no membrane	Pt/Nb plate (95% Pt)	Pt/Nb plate (95% Pt)	CO_2 , CH_3OH + [bmim][Br] + CH_3OK	CH_3OH + [bmim][Br] + CH_3OK	DMC	-	Undivided cell: 80.85 mM; FAB membrane: 9.74 mM	-	[36]
Nafion® 117	Sn-GDE	DSA	CO_2 , KCl + $KHCO_3$	aq. KOH	HCOOH	---	FE HCOOH= 70 % (1348 mg/L)	1 / 25	[40]
Nafion® 117	Sn-GDE	Pt foil	CO_2 , $KHCO_3$	Water	HCOOH	-1.8 V	FE HCOOH= 78 %	- / 25	[41]
Selemion™ (CEM)	Net Ag-electrode	Pt plate	CO_2 , KCl	aq. KCl	CO, H_2	-	$AgNO_3$ added to the electrolyte). FE CO> 45 %	-	[42]
Nafion®	Sn-GDE + PTFE	Pt foil	CO_2 , $KHCO_3$	aq. $KHCO_3$	HCOOH	-1.8 V	FE HCOOH= 87 %	- / 25	[43]
Nafion® 117	Pt NP-CNT	Pt rod	CO_2 , $KHCO_3$	aq. $KHCO_3$	HCOOH, CH_3COOH	-	HCOOH= $2.3x10^{-4}$ M; CH_3COOH= $1.8x10^{-4}$ M	- / 25	[46]
Nafion® 117	Ag - Graphite GDL	Pt black NP	CO_2, [emim][Br]	aq. H_2SO_4	CO, H_2	-1.5 V	FE CO> 9 % (H_2 balance)	- / 22	[47]
Nafion® 117	Ag NP	Pt NP	CO_2, Aq. [bmim][BF_4]	aq. H_2SO_4	CO	-	FE CO~ 100 % when 89.5 mole% water was added to the [bmim][BF_4]	-	[49]
Selemion™ (AEM)	Cu mesocrystals	Pt mesh	CO_2 , $KHCO_3$	aq. $KHCO_3$	HCOOH, CH_4, C_2H_4, CO, H_2	-1.4 to -0.9 V	FE C_2H_4= 27.2 %; HCOOH= 17.5 %; CO= 7.5 %; CH_4= 2.7 %	-	[54]
Nafion® 961 and Nafion® 430	Pb plate	IrO_2/Ta_2O_5	CO_2 , K_2HPO_4 + H_3PO_4	Aq. KOH	HCOOH	2 $mAcm^{-2}$	FE HCOOH= 93 % HCOOH at 2 mA/cm^2. HCOOH concentration increases with CD (max.= 0.016 M)	1 / 25	[58]

Nafion®	Electrocatalysts: Cu, CuO, ZnO, Mo_2C, Co_3O_4	Pt/C (40% wt)	CO_2, $KHCO_3$ or KOH or DMF	Water	-	-	Cu, CuO, ZnO, Co_3O_4 actives catalysts in the protocol	1 / 25	[59]
Nafion® 112	Cu NWs or Cu NNs	Pt foil	CO_2 , $KHCO_3$	aq. $KHCO_3$	CH_4, C_2H_4, HCOOH, H_2	-1.5 to -1.1 V	Cu NWs: FE C_2H_4= 12%; Cu NNs: FE CH_4= 14 % and HCOOH= 48 %	- / 10	[60]
Selemion™ (CEM)	Cu	-	CO_2 , $KHCO_3$	aq. $KHCO_3$	CH_4, C_2H_4, CO, HCOOH	-1.64 V	FE CH_4= 33.3 %; C_2H_4= 25.5 % at -1.44V and 5 mA/cm^2	- / 19	[61]
CEM	Crystal Cu	-	CO_2 , $KHCO_3$	aq. $KHCO_3$	CH_4, C_2H_4, CO, HCOOH, H_2, alcohols	-1.75 V	Cu (110): FE CH_4= 49.5 %; C_2H_4= 15.1 %	- / 18	[62]
Nafion® 117	Sn-GDE	DSA	CO_2 , KCl + $KHCO_3$	aq. KOH	HCOOH	-2 V / 90 mAcm^{-2}	FE HCOOH=70 % (1519 mg/L)	1 / 25	[63]
Selemion™	Cu NP over glassy carbon	-	CO_2 , $NaHCO_3$	aq. $NaHCO_3$	CH_4, H_2	-1.55 V	FE CH_4= 76 %	1.2 / 25	[64]
Nafion® 112	Cu_2O electrodeposited	Pt mesh	CO_2 , $KHCO_3$	aq. $KHCO_3$	CH_4, C_2H_4, H_2, CO, HCOOH	-1.9 V	FE CH_4= 21 %; C_2H_4= 11 %; H_2= 50 %	1 / -	[65]
Nafion®	Cu foil	Pt mesh	CO_2 , $KHCO_3$	aq. $KHCO_3$	CH_4, C_2H_4, H_2, CO	-1.65 to -1.4 V	FE CH_4= 0-70 %; C_2H_4= 0-35 %; H_2= 10-95 %; CO= 0-13%	-	[66]
Nafion®	Fe NP over GDL	Pt wire	CO_2 , $KHCO_3$	aq. $KHCO_3$	HCOOH, CH_3COOH, CH_3OH	**1 V	Global productivity: 1.75x10^{-2} mmole/h	- / 25	[67]
Selemion™ (AEM)	Cu_2O-derived Cu	Pt wire	CO_2 , $KHCO_3$, $PdCl_2$	aq. $KHCO_3$	C_2H_6, H_2, alcohols, CH_4, C_2H_4, CO	-1.2 V	FE C_2H_6= 30 %; H_2= 15 %; alcohols< 15 %; CH_4, C_2H_4 and CO= traces	-	[68]
Selemion™ (AEM)	Cu_2O layers into Cu disc	Pt wire	CO_2 , $KHCO_3$	aq. $KHCO_3$	C_2H_4, H_2, C_2H_5OH, CH_4, CO, HCOOH	-1.2 V	FE C_2H_4= 39 %; H_2~ 50 %; rest of products< 10 %	-	[69]

* Ref. electrode: Pb(Hg)x/$PbSO_4$/SO_4^{2-}

** Difference of 1 V between electrodes

4.1.1. L-L ecMRs based on CEMs

CEMs have been widely used in ecMR systems due to their enhanced properties for the transport of protons. Among the available materials, Nafion® is typically applied. A number of value-added products, on dependence of the electrocatalytic materials applied, can be found in the literature as described hereafter.

<u>Ag-based electrodes</u>

In the first group, silver cathodes have been commonly used for CEM-based systems [11, 42, 47-49]. In this regard, Delacourt et al. [11] studied different reactor configurations for the electrochemical reduction of CO_2 to syngas (CO + H_2). A Nafion® membrane was used in a L-L ecMR to form a MEA. The catalytic layer consisted in acetylene black carbon and a polymer of the same nature, together with Ag catalyst. The experiments were carried out at 20 $mA \cdot cm^{-2}$ with a cathode potential of -1.42 V vs. SCE. A CO formation efficiency of 40% was achieved. In the same way, other researchers have also used different CEMs for the electrochemical reduction of CO_2 to syngas [42, 47-49].

Rosen et al. [47] applied a sandwich style reactor with two liquid and gas channels with a Nafion® 117 membrane. An Ag nanopowder ink supported on Sigracet graphite GDL was used. The ionic liquid [emim][Br] was used as catholyte, obtaining a *FE* to CO higher than 96 % as a function of the potential cell applied. Besides, *FE* to H_2 formation was very low. The *EE* observed ranged between 50 % to 90 % at 1.5 V. Salehi-Khojin et al. [48] also used a Nafion® membrane in a L-L ecMR. The rate for CO_2 conversion was about 10 times higher on 5 nm Ag nanoparticles (NP) than on a bulk Ag electrode.

Moreover, Rosen et al. [49] also used Ag NP and the ionic liquid [emim][BF_4] for the electroreduction of CO_2. They showed that the addition of water to the ionic liquid

increased the efficiency for CO_2 conversion to CO. The maximum *FE* to CO achieved in this system was nearly 100 % when 89.5 mol% water was added to the ionic liquid. Besides, Yano et al. [42] used a Selemion™ CEM to separate the cathode and anode compartments, with a GLS (gas-liquid-solid)/Ag electrode and 0.5 M KCl. The effect of the pH was studied. The *FE* to CO was higher than 45 % using a GLS-Ag electrode. Besides, a CO conversion near 100 % was observed when $AgNO_3$ was added to the electrolyte at pH=3.5, concluding that *FE* decreased as the pH increased.

Overall, it seems that an appropriate catholyte and pH conditions are crucial for an enhanced CO_2 electrochemical conversion. Besides, the application of highly conductive ionic liquids for the reduction process seems to be beneficial [70]. The use of CEMs for the electrochemical reduction of CO_2 to CO in Ag-based electrodes in combination with ionic liquids as electrolytes showed *FEs* to CO near to 100 %.

Cu-based electrodes

Moreover, several authors reported the application of Cu-based catalysts in combination with CEMs for the electrochemical reduction of CO_2 into valuable products [21, 23, 26, 28, 29, 31-35, 46, 59-62, 64-66, 71]. The conversion efficiencies have been found to be directly linked to the type of Cu catalyst used in the working electrode (Cu foil, Cu mesh, Cu NP, etc).

Ogura et al. [71] describe a Cu mesh in order to evaluate the influence of different potassium halides (KCl, KBr and KI) as catholytes at pH=3. A Nafion® 117 membrane was used to divide the anode and cathode compartments. They concluded that the presence of Cu-halide anions facilitated the electron transfer and the current density. The reduction of CO_2 increases in the following order $Cl^- < Br^- < I^-$. A tinned-Cu mesh cathode together with a Nafion® 450 membrane has also been proposed to electroreduce

CO_2 to HCOOH, H_2, CO and CH_4 in L-L ecMR [23] with a pure CO_2, or a mixture of CO_2 and N_2, in gas phase combined with a 0.45 M $KHCO_3$ catholyte. The experiments were carried out near ambient conditions and over a *CD* range of 22 to 178 $mA \cdot cm^{-2}$. The *FE* achieved for each product in the factorial design of experiments carried were 23-71 % to HCOOH, 24-86 % to H_2, 0-5 % to CO and 0-0.3 % to CH_4. They also showed that current efficiency increases with CO_2 concentration. The maximum *FE* to HCOOH (*FE*= 86%) was obtained at 22 $mA \cdot cm^{-2}$. Kas et al. [28] used a three-electrode assembly in order to analyse the catalytic activity for the electrochemical reduction of CO_2 to hydrocarbons. Cuprous oxide films were electrodeposited onto Cu plates as working electrodes, with a Nafion® 112 membrane separating the cathode and anode compartments. A 0.1 M $KHCO_3$ solution (pH= 6.8) was used as catholyte with CO_2 gas to produce CO, CH_4, C_2H_4 and C_2H_6 at a *FE* of 0-4%, 1-5%, 20% and 2.5%, respectively, at an applied voltage of -1.1 V vs. RHE.

Gonçalves et al. [31, 32] evaluated a Cu mesh and a modified Cu electrode for the reduction of CO_2. The Cu-modified materials showed and improved efficiency for the electrochemical reduction of CO_2 to hydrocarbons, in comparison to a Cu mesh, with a *FE* has high as 33% and 10% for C_2H_4 and CH_4, respectively. Manthiram et al. [64] demonstrated that well-dispersed Cu NP over glassy carbon (working electrode) show high *FEs* to CH_4 from CO_2 reduction using a two-compartment flow cell. A Selemion™ membrane separated the working and counter electrode compartments, which are filled with an aqueous solution of 0.1M $NaHCO_3$. A *FE* to CH_4= 76 % was obtained at -1.55 V vs. Ag/AgCl, higher than the obtained values at Cu foils for the same conditions (*FE*~ 40 %). The authors suggested that these prepared Cu-electrodes may help to achieve enhancement for the electrochemical reduction of CO_2 to CH_4, minimizing polarization losses and maximizing the energy efficiency.

Moreover, Kas et al. [65] suggested that the concentration of the electrolyte could strongly affects the selectivity of the electrochemical reduction of CO_2 to hydrocarbons. Cu-NP over Cu substrates were used as working electrodes in a two-compartment stainless-steel autoclave reactor, in which a Nafion® 112 membrane divided the cathode and anode (Pt mesh) compartments. A 0.5 M $KHCO_3$ aqueous solution allows to obtain *FEs* of 21 %, 11 % and 50 % to CH_4, C_2H_4 and H_2, respectively, at -1.9 V vs. Ag/AgCl and 1 atm. However, decreasing the electrolyte concentration to 0.1 M results in increased *FE* to C_2H_4 (36 %) in the same conditions. Besides, C_2H_4 formation is additionally favoured by increasing CO_2 pressure to 9 atm. From these results, it can be concluded that the concentration of the electrolyte has an important effect in the selectivity of the electrochemical reduction of CO_2 into hydrocarbons. The same idea was supported by Varela et al. [66] in an H-type cell divided by a Nafion® membrane using the same electrolyte (aq. $KHCO_3$ solution). A Cu foil and a Pt mesh were used as working and counter electrodes, respectively. The maximum *FE* to CH_4 (70 %) was obtained at -1.6 V vs. Ag/AgCl, applying a 0.2 M $KHCO_3$ concentration as electrolyte. According to the work developed by Kas et al. [65], electrolytes with high buffer capacity (i.e. high $KHCO_3$ concentration) increase *FE* to CH_4 and H_2 over C_2H_4. They also add that C_2H_4 formation is not affected by local pH at low overpotentials (proton/electron transfer is not the rate determining step in the formation process).

Kaneco et al. used a Cu foil as cathode with different sodium salts in CH_3OH [33] or LiOH [26]. A Nafion® 117 membrane was used in both cases to separate the cathode and anode sides, and high negative V vs. Ag/AgCl were applied to the cell. When a $NaClO_4$ /CH_3OH mixture was used as electrolyte [33] the *FE* to CH_4 was 70.5 % at -3 V. In the second case [26], the *FE* to CH_4 + C_2H_4 was as high as 78 % at -4 V. The positive effect of sodium salts in CH_4 selective production was then proven. Aydin et al.

[34] used a Cu wire with polypyrrol-coated electrocatalyst. A lithium salt ($LiClO_4$) in methanol was used as catholyte with a Nafion® 117 membrane separating the chambers. High-pressure experiments (10, 20, 40, and 60 bars) in a CO_2 atmosphere were performed. At 20 bar, *FE* was as high as 25.5 % and 3.1 % for CH_4 and C_2H_4, respectively. Other different products such as CO, HCOOH and acetic acid were also detected with a *FE* of 15.1 %, 22.1 % and 40.2 %, respectively. Yano et al. [35] used a CEM (Selemion™) and a Cu mesh or Cu (I) halide-confined mesh with the same catholyte and anolyte based on aqueous potassium halides. The study seeks to analyse the influence of different Cu-halides electrodes at -2.4 V vs. Ag/AgCl applied potential. The CuBr electrode presented higher *FE* to C_2H_4 when KBr was used as electrolyte (*FE*= 79.5 % and 5.8 % to C_2H_4 and to CH_4, respectively). CuI and CuCl have been also used as electrodes in this system, and the *FE* to C_2H_4 in each case was 72.8 % and 60.5 %, respectively. The study showed that Cu halide-confined meshes enhance the *FE* to C_2H_4 in comparison to a Cu mesh electrode (*FE* of 40% to C_2H_4 in KCl solution).

Xie et al. [60] used a two compartment cell based on modified Cu electrodes (Cu nanowires or Cu nanoneedles), 0.1 M $KHCO_3$ as electrolyte and a Nafion® 112 membrane to separate the compartments. Cu nanowires presented better results in terms of *FE* to C_2H_4 (12% at -1.3 V vs. RHE) whereas Cu nanoneedles led to the highest *FE* to CH_4 (14 % at -1.2 V) and to HCOOH (48 % at -0.9 V). Hori et al. [61, 62] also used a CEM to separate the cathode and the anode in L-L ecMRs. The performance of different metal electrodes as cathode catalyst [61] and different Cu single crystal electrodes [62] were studied to analyse their influence in CH_4 and C_2H_4 production. The highest *FE* was observed for a Cu electrode at -1.44 V vs. NHE at 5 $mA \cdot cm^{-2}$ (33.3 % CH_4 and 25.5 % C_2H_4) [61]. In a second study [62], higher *FEs* to CH_4 were achieved when a Cu (110) electrode was used (49.5% CH_4 and 15.1% C_2H_4 at -1.55 V and 5 $mA \cdot cm^{-2}$). The

influence of *CD* in the *FE* to hydrocarbons was also tested. At low current densities (2.5 $mA \cdot cm^{-2}$), the *FE* to hydrocarbons dropped, so high *CDs* were needed in these systems. Higher *FE* to CH_4 and to C_2H_6 were observed in an H-type electrochemical cell divided by a glass frit [72] using pure or electrodeposited Cu, which were carried out in $CuSO_4$ 0.25M (Cu/Cu-H) or 0.025 M (Cu/Cu-L) baths. Results with a pure Cu electrode showed that *FE* to CH_4 was about 28 % at -1.2 V and *FE* to C_2H_6 was about 15 % at -1 V. The highest *FE* to C_2H_6 in this work was achieved on Cu/Cu-L electrodes with a value about 43 % at -1.2 V. When a Cu/Cu-H electrode was used, a *FE* to CH_4 and to C_2H_6 about 20 % and 27 %, respectively, was observed at -1.2 V [72].

Ampelli et al. [46] studied the influence of the phase used in the cathode in order to carry out a comparison in terms of productivity and type of products at the same conditions (electrodes and reaction). In these reactors, a Nafion® membrane was used to separate the compartments and different metal NP such as Co, Cu, Fe and Pt were supported over functionalized carbon nanotubes (CNTs) or commercial carbon black (CB), forming a GDE as represented in Figure 8. The differences between the systems are the type of electrolyte at the anode compartment ($KHCO_3$ in L-L ecMR and KCl in G-L ecMR).

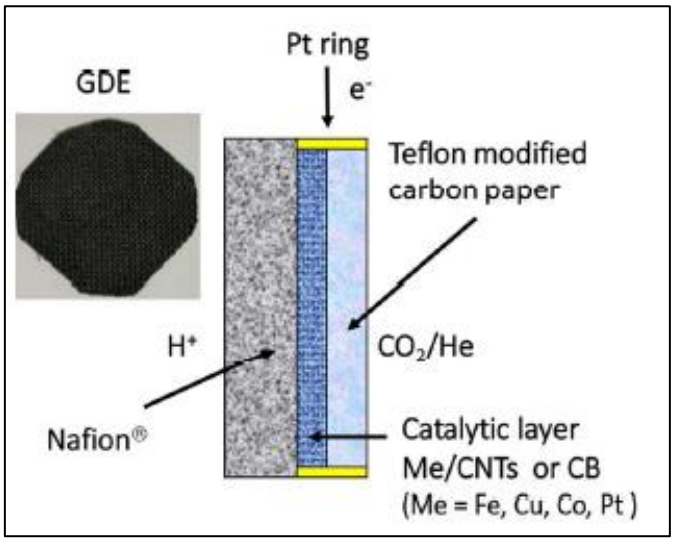


Figure 8. Representation of the GDE used for CO_2 electrochemical reduction in the work from Ampelli et al. [46]. Reproduced with permission from ref. [46].

Different products were detected in each configuration. HCOOH, acetic acid and CH_3OH were obtained as traces in the L-L ecMR. In addition, the order of product formation was on dependence of the metal catalyst applied: Pt-CNT ~ Fe-CNT > Cu-CNT > Fe-carbon black in the L-L ecMR. In addition, the reaction mechanisms were analysed in both cases [46]. The absence of the electrolyte and the higher CO_2 concentration at the catalyst surface could inhibit the mechanisms for electron transfer, favouring the CO_2 dissociation to CO at the different metals used as catalyst.

Yim et al. [29] studied the influence of the membrane in a L-L ecMR using CH_3OH as a solvent. A Cu plate was used as cathode, and a Nafion® 117 membrane for CH_4 production. The results showed that the electrochemical cell without membrane presented better results (*FE*= 35.6% to CH_4) in comparison to the system with the Nafion® membrane.

Albo et al. [21] studied the electrochemical reduction of CO_2 into CH_3OH using Cu_2O and Cu_2O/ZnO-catalyzed carbon papers. A Nafion® 117 membrane was also used to separate the cathode and anode compartments. When a Cu_2O-carbon paper electrode was used, a *FE* to CH_3OH of 45.7 % was achieved, but a rapid deactivation of the material occurred. In any case, a stable modest *FE* of 17.7 % was obtained is Cu_2O/ZnO (1:1)-based systems at -1.3 V vs. Ag/AgCl, so the use of Cu_2O-ZnO mixtures for the continuous electrochemical CO_2 reduction to CH_3OH showed promise. Recently, the technical possibilities for the electrochemical reduction of CO_2 into CH_3OH has been reviewed [73].

Regarding the possibility of suppressing the liquid phase from the catholyte (to avoid transfer limitation due to the low solubility of CO_2 in water), Genovese et al. [67] made a comparison between liquid (L-L ecMR) and gas (G-L ecMR) conditions in the production of fuels from CO_2 reduction. Different metallic NP (Fe or Cu) supported on GDL were tested as working electrodes, whereas a Pt wire was used at the anode side. A CEM (Nafion®) divided the cell compartments filled with a 0.5 M $KHCO_3$ solution in the anode side. Alcohols and traces of hydrocarbons were observed in gas-phase studies, while liquid phase experiments mainly produced HCOOH, CH_3COOH and traces of CH_3OH. As a conclusion, liquid phase CO_2 reduction allowed to achieve higher productivity values ($5x10^{-3}$ mmol·h^{-1} in liquid phase over $1.5x10^{-4}$ mmol·h^{-1} in gas phase, using Cu-GDL-based catalyst), minimizing also the HER.

As can be deduced from the discussion above, the catalyst plays a main role in the electrochemical reduction of CO_2, so a correct catalyst selection for each process is essential. For this purpose, Singh et al. [59] developed a catalytic activity protocol for the electrochemical reduction of CO_2. Different electrocatalysts (Cu, CuO, ZnO, Mo_2C and Co_3O_4) were supported into a GDL, forming the cathodes. A Nafion® membrane was sandwiched between the electrodes and different studies such as cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out, whilst the cathode side of the reactor was fed with CO_2 saturated 0.5 M $KHCO_3$ solution. As conclusion, Cu, CuO, ZnO and Co_3O_4 were actives in the proposed protocol for the electrochemical reduction of CO_2.

In conclusion, Cu-based electrodes have been widely used as cathodes. It seems that nanomaterial-based electrodes may enhance the electroreduction of CO_2 to hydrocarbons (mainly CH_4 and C_2H_4) [64]. Besides, electrolyte type and its concentration seem to be crucial for an efficient CO_2 electroreduction process. Finally,

the utilisation of Cu-halides meshes is favourable, attending to the high *FE* to C_2H_4 (79.5 %) in L-L ecMRs divided by a CEM, in comparison to the *FE* achieved on Cu-mesh electrodes [35].

Sn and Pb-based electrodes

Many authors have focused their research on the utilisation of tin and lead catalysts for the electroreduction of CO_2 using L-L ecMRs [10, 20, 24, 40, 41, 43, 58, 63] with the aim of producing HCOOH with high *FEs*. Kopljar et al. [10] studied the feasibility of the electrochemical HCOOH production within an industrial environment. A proton conductive membrane (Nafion®) to separate the cathode and anode chamber was used and both chambers were filled with an aqueous solution of $KHCO_3$. High *FE* (> 80 %) was obtained at 200 $mA \cdot cm^{-2}$ and pH= 10, whereas the *FE* for CO and H_2 was approximately 10 %. A maximum *FE* of 93 % to HCOOH was achieved at 50 $mA \cdot cm^{-2}$. In the same way, Wang et al. [41] carried out different electrochemical measurements such as CV and electrochemical and impedance spectroscopy (EIS), in order to analyse the *FE* to HCOOH formation. The electrolyte was a $KHCO_3$-based solution in a wide range of concentrations. When a concentration of $KHCO_3$ equal to 0.5 M is used, a maximum *FE* of 78 % to HCOOH was achieved at an applied potential of -1.8 V. Wang et al. [43] reached performance enhancements by adding polytetrafluoroethylene (PTFE) into the catalyst layer. This makes possible to increase the catalytic surface area and CO_2 diffusion. The highest *FE* was around 87 % at -1.8 V vs. Ag/AgCl when 11.1 wt%. of PTFE was added, improving the *FE* to HOOCH to a value of 25.4 %. As can be noticed in these studies, the type and concentration of the electrolytes have a great influence on the maximum achieved *FE* that could be achieved. Besides, improvements in the catalyst layer by adding different compounds are also an interesting approach.

Moreover, Alvarez-Guerra et al. [20] used a Pb plate as cathode and a solution of 0.45 M $KHCO_3$ + 0.5 M KCl as catholyte. The highest *FE* to HCOOH achieved was 94.7 % at low current density values (2.5 $mA \cdot cm^{-2}$) with a measured concentration of 14.4 $mg \cdot L^{-1}$. At the same conditions, a Sn plate was used as working electrode to compare the performance of the process in terms of rate of HCOOH production and *FE* [24]. With a Sn cathode, the rates for HCOOH production were 25 % higher with efficiencies around 70 %. Considering these results, Del Castillo et al. [40] applied GDEs loaded with Sn particles with the aim of operating at higher *CD*. This Sn-GDE configuration led to higher concentrations (885 and 1348 $mg \cdot L^{-1}$), maintaining an efficiency of about 70 %. One year later, Del Castillo et al. [63] analysed the effect of metal loading and Sn-particle size in Sn-GDE electrodes in order to improve HCOOH formation rates. The best results were observed with a catalytic loading of 0.75 mg $Sn \cdot cm^{-2}$ and a particle size of 150 nm, achieving *FEs* around 70 % to HCOOH at 90 $mA \cdot cm^{-2}$, with rates and concentration over 3.2 $mmol \cdot m^{-2}\ s^{-1}$ and 1.5 $g \cdot L^{-1}$, respectively. They concluded that the use of smaller Sn-NP (< 150 nm) and carbon supports for the electrochemical reduction of CO_2 to HCOOH might allow further improvements in the process.

The utilisation of Pb-based catalyst as cathodes for the electroreduction of CO_2 to HCOOH in L-L ecMRs has been also considered by Subramanian et al. [58], in which the anode and the cathode chambers were separated by a composite perfluoro polymer CEM. CO_2 was absorbed in a 0.2 M K_2HPO_4 + H_3PO_4 solution, which was fed to the cathode chamber, obtaining a maximum *FE* to HCOOH of 93 % at 2 $mA \cdot cm^{-2}$. They also showed that HCOOH concentration increases with *CD*. The highest measured value was 0.016 $mol \cdot L^{-1}$ (1085 $mg \cdot L^{-1}$), which is in the range of those concentrations obtained by Del Castillo et al. [40] using DSA as anode. It should be remarked that the utilisation of GDEs led to high *FE* when Sn and Pt are used as cathode and anode

catalysts, respectively. In order to analyse the viability of HCOOH production from CO_2 electroreduction, Dominguez-Ramos et al. **[**74**]** studied the global warming footprint associated to the process, identifying different scenarios and concluding that the requirements of energy and materials are too high to ensure a sustainable production of HCOOH from CO_2 electroreduction and thus, future technical advances are required.

In general, Sn-based catalysts allow obtaining HCOOH from CO_2 reduction with higher *CDs* when compared to Pb-based catalyst, even though Sn-based catalysts have been commonly used for this process, as found in literature. Besides, the modification of the catalyst layer by adding different compounds, the utilisation of GDEs based on NPs and alterations in the electrolyte may enhance the *FE* and concentration of HCOOH at the reactor outlet.

Pt-based electrodes

In addition, Pt-based catalysts have been used for the electrochemical valorisation of CO_2 in L-L ecMRs for DMC synthesis [30] and CO_2 electroreduction to HCOOH [25]. Garcia-Herrero et al. [30] used a Pt/Nb plate (95 % Pt) with 200 mL of CH_3OH in combination with the ionic liquid [bmim][Br] and potassium methoxide as electrolyte. A Nafion® 117 membrane was used. A concentration of 11.37 mM was achieved when the electrolyte is formed by 80% CH_3OH, 15% ionic liquid and 5% CH_3OK. On the other hand, Tamilarasan et al. [25] used a glassy carbon electrode with a Pt catalytic loading of 1 mg cm^{-2} at the cathode in a 0.5 M $KHCO_3$ solution. A polymer electrolyte membrane was applied and the influence of operation mode in the cell (continuous or discontinuous) was evaluated for HCOOH production at ambient conditions. The results showed that higher concentrations can be obtained (almost double) in a continuous operation mode (0 to 35 $mmol \cdot L^{-1}$) in comparison to 18 $mmol \cdot L^{-1}$ in a discontinuous operation mode.

In conclusion, many researchers used CEMs, in particular Nafion® membranes, for the electrochemical reduction of CO_2 in L-L ecMRs. Most of the anodes studied are based on Pt plates. However, different catalyst materials and electrolytes at the cathode compartment have been tested depending on the desired product. High *FEs* to HCOOH and CO have been achieved using CEMs, whereas further studies seems to be needed in order to achieve higher *FE* and concentrations for the formation of hydrocarbons using ecMRs.

4.1.2. L-L ecMRs based on AEMs

Materials based on Ag, Cu and Pt have been widely used as working electrodes for the electrochemical reduction of CO_2 in order to obtain CO, hydrocarbons and DMC, respectively, using AEMs in ecMRs. Besides, Pt has been commonly reported as anode in these systems [19, 27, 36, 54, 68, 69].

Hatsukade et al. [19] studied the electrochemical reduction of CO_2 on silver surfaces. In this work, an Ag foil was used as cathode, and an AEM was placed between the electrodes to mitigate the transport of liquid products from the working to the counter electrode. A solution of 0.1 M $KHCO_3$ was utilized as electrolyte (pH= 6.8 at the catholyte) and a voltage range of -0.6 to -1.42 V vs. RHE was applied to the cell. CO and H_2 were the main products obtained, with also HCOOH, CH_4, CH_3OH and C_2H_5OH. The *FE* range for H_2, CO, HCOOH and other products formation were 10-100 %, 5-90 %, 2-8 % and < 0.1 %, respectively. A *FE*= 90 % to CO was achieved at -1.1 V vs. RHE, whereas a *FE*= 8 % to HCOOH was obtained at -1.4 V vs. RHE.

Regarding Cu-based catalysts, Kuhl et al. [27] tested a Cu foil in order to analyse the multicarbon products formed from CO_2 electroreduction, being 16 the different products observed such as CH_4, C_2H_4 and HCOOH, together with ethylene glycol,

glycoladehyde, hydroxyacetone, acetone or glyoxal, that are not commonly as CO_2 electroreduction products. A *FE* of 40 % to CH_4 was achieved at -1.15 V, whereas C_2H_4 and HCOOH were detected with a *FE* of 25 % at -1.05 V and 23 % *FE* at -0.87 V, respectively. Besides, Chen et al. [54] applied different Cu-based catalysts (Cu mesocrystals, Cu NP and electropolished Cu) for the electroreduction of CO_2 in an aqueous solution of $KHCO_3$. The highest *FEs* were achieved when applying Cu mesocrystals, with values of 27.2 %, 17.5 %, 7.5 % and 2.7 % for the production of C_2H_4, HCOOH, CO and CH_4, respectively at different potentials.

In addition, Chen et al. [68] evaluated the influence of electrolyte conditions using Cu_2O-derived Cu catalyst in order to electroreduce CO_2 to C_2H_6 in a three-electrode cell with a 0.1 M $KHCO_3$ solution, when an AEM (Selemion^{TM}) separated cathode and anode compartments. The *FE* to C_2H_4 was 30 % at -1.2 V vs. Ag/AgCl, while traces of C_2H_6 were observed. The other products obtained were H_2, HCOOH and alcohols.

Besides, adding $PdCl_2$ (100 mg) to the electrolyte at the same operation conditions, produced increases in the *FE* to C_2H_6, with values of 30 % at -1.2 V vs. Ag/AgCl. They proposed that C_2H_4 is firstly produced from CO_2 reduction at Cu sites. Afterwards, the hydrogenation of C_2H_4 with the assistance of $PdCl_2$ occurs to produce C_2H_6. By contrast, other Pd-based particles were also tested, but did not reach the same conversion efficiencies. Ren et al. [69] also tested Cu_2O-based catalysts in an electrochemical cell divided by an AEM in order to study the *FEs* to C_2H_4 and C_2H_5OH in a 0.1 M $KHCO_3$ solution. In this way, Cu_2O layers deposited onto a Cu disc, and a Pt wire were used as working and counter electrodes, respectively. The influence of the Cu_2O layers was also discussed, concluding that 1.7-3.6 μm thickness led to the best *FE* to C_2H_4 and C_2H_5OH at -1.2 V vs. Ag/AgCl, with values of 34-39 % and 9-16 %, respectively. In these conditions, the *FE* to CH_4 was < 0.1 %. Therefore, it can be

concluded that the *FE* to C_2 products can be systematically tuned by varying the thickness of Cu_2O overlayers.

As discussed in another section, Garcia-Herrero et al. [36] studied the influence of the applied membrane in the electrochemical synthesis of DMC from CO_2. For this purpose, an AEM and a Pt/Nb (95 % Pt) plate as working electrode was applied. The maximum concentration achieved for DMC was 9.74 $mmol \cdot L^{-1}$. The best results were obtained without membrane in which the DMC concentration was 80.85 $mmol \cdot L^{-1}$, following by that concentration obtained when using a Nafion® CEM (11.37 mM). The better performance in the absence of membrane was explained by mass transport enhancements, although the presence of the ionic liquid [bmim][Br] was also required to reach those values. Yim et al. [29] reached the same conclusion when no membrane was applied in their system. In any case, the application of an undivided cell makes difficult the separation of reaction products and thus, increases the cost associated to the process.

Overall, the utilisation of AEMs rather than CEMs to divide the ecMR is gaining importance due to the advantages of reducing polarization losses. Besides, high *FE* to CO (90 %) has been achieved in Ag-based catalysts, which is comparable to the *FEs* observed in some cases in which CEMs have been tested. Regarding the utilisation of Cu-based catalysts, C_2H_4 has been obtained with Cu_2O and AEMs with acceptable *FEs* (~ 30-40 %). Besides, C_2H_6 and C_2H_5OH have been also produced, where the thickness of the Cu_2O layers seem to be critical in order to enhance efficiency.

As a result, further developments in terms of catalyst materials and electrolytes are necessary to achieve the desired products with high *FEs*.

4.2. Gas-Liquid (G-L) ecMRs

Table 2 summarizes the different experimental conditions, catalytic materials, main products and performance results for the use of G-L ecMRs in CO_2 electroreduction processes. As for L-L ecMRs, CEMs are the common alternative to separate the cathodic and the anodic compartments in these systems [11, 12, 17, 45, 46, 50, 52, 53, 55-57, 75, 76].

4.2.1. G-L ecMRs based on CEMs

Regarding the use of CEMs in G-L ecMRs, Delacourt et al. [11] used an integrated system with a buffer layer between the Ag catalytic layer and the membrane for the reduction of humidified CO_2. An enhanced selectivity for CO_2 reduction to CO was observed, since the buffer layer probably prevented an excessive amount of protons reaching the cathode. In fact, the *FE* to CO increases up to 80 % when a pH-buffer layer of $KHCO_3$ was used. In addition, Wu et al. [50] studied the influence of a $KHCO_3$ buffer layer placed between the cathode and a Nafion® membrane in a G-L configuration at pH= 7 when using a Sn-based GDEs. The onset potential for HCOOH production was observed at -1.2 V and the *FE* was as high as 70 %. A high cell potential was needed in order to overcome the anodic overpotential required for water oxidation. It seems that buffer layers can be utilized to enhance the formation of CO and HCOOH, increasing *FEs*. The pH and concentration of the buffer layer are also essential to achieve high *FEs* in both systems.

Table 2. Experimental conditions, catalytic materials, main products and significant results for CO_2 valorisation in G-L ecMRs.

Membrane	Cathode	Anode	Catholyte	Anolyte	Products	V vs. Ag/AgCl / CD ($mAcm^{-2}$)	Main results	P (atm) / T (^oC)	Ref.
Nafion®	Ag	Pt-Ir (1:1) alloy	Humidified CO_2 gas	Pure water/$KHCO_3$	CO, H_2	-1.38 V	FE CO= 82 % with buffer layer	1 / 25	[11]
Sterion® (CEM)	Cu powders in carbon nanotubes (CNTs)	IrO_2 over carbon paper	CO_2 gas	H_2O saturated N_2	C_2H_4O, methyl-HCOOH, CH_4	-30 mA	Selectivity: C_2H_4O= 70 %; methyl-HCOOH= 13 %; CO= 10 %; CH_4= 7 %	1 / 90	[12]
Nafion® 117	Fe or Pt over CNTs	Pt wire	CO_2 gas	aq. KCl	Alcohols and hydrocarbons (traces)	2 V	Fe-CNTs presents better performance	1 / 60	[17]
PEI and QPEI doped with KOH (AEM)	Cu_2O on porous carbon paper	Pt/C	CO_2 gas	Deionized water	CO, H_2, CH_4, C_2H_4, C_2H_6	* Cell potential: 1.8 to 3 V	FE CH_4= 6-11 %; C_2H_4= 3-20 %	1 / 25	[22]
Nafion® 115	Pt or Fe doped TPE-CMP/CNTs	Pt wire	CO_2 gas	aq. $KHCO_3$	C_1-C_8 oxygenates.	-1.5 V	Highest productivity: 70 % Pt/TPE-CMP + 30 % CNTs ($7.2x10^{-5}$ $mmol{\cdot}h^{-1}$).	- / 60	[45]
Nafion® 117	Metal NP on CNT/GDL	Pt wire	CO_2 gas	aq. KCl	CO, H_2, CH_3OH, C_2H_4O, C_2H_5OH, acetone, C_3H_8O, CH_3COOH.	-	Fe-CNT/GDL: best productivity ($4.8x10^{-4}$ $mmol{\cdot}h^{-1}$)	- / 25	[46]
Nafion® with buffer layer	Sn ink + GDL	Pt/C spray + GDL	CO_2 gas	aq. KOH	HCOOH, CO, H_2	-1.2 V	FE HCOOH= 70 %	1 / 25	[50]
AEM	Silver-coated	Pt plate	CO_2 gas	aq. K_2SO_4	CO, HCOOH, H_2	-1.51 V / 20 $mAcm^{-2}$	FE CO= 92.1 %	1 / -	[51]
Nafion® 115	Cu foil	Pt flag	Humidified CO_2 gas	aq. H_2SO_4	CH_4, C_2H_4	-1.95 V	FE CH_4= 8 %; C_2H_4= 10 %	- / 22	[52]
Nafion®	Cu-solid polymer electrolyte	Pt mesh	CO_2 gas	aq. K_2SO_4	CH_4, C_2H_4, CO, H_2, HCOOH	-1.45 V	FE H_2> 89 %	- / 22	[53]
Nafion®	Cu on porous carbon	Pt/C (40 % wt Pt)	CO_2 gas	Alkali doped PVA	CH_3OH, HCOH, CH_4	* Cell potential: 2 V	FE CH_4= 4.5 %; CH_3OH and HCOH < 1%	1 / 25	[55]
Glass frit	Sn-GDL	Pt wire	CO_2 gas	aq. $NaHCO_3$	HCOOH	-1.8 V	FE HCOOH= 70 %	-	[56]
AMI-7001	Cu_2O on porous	Pt/C (40%	Humidified	water	CH_4, C_2H_4,	-2.7 to -2.2 V	FE CH_4= 30 %; CH_3OH= 20	1 / 25	[57]

(AEM)	carbon paper	wt Pt)	CO_2 gas		CH_3OH, H_2		%; C_2H_4= 15 %		
Nafion®	TPE-CMP doped with metal NP	Pt wire	CO_2 gas	aq. $KHCO_3$	Hydrocarbons, C_2H_4O, H_2, alcohols	-	Hydrocarbon traces	- / 60	[75]
Nafion® 115	GDM-Fe metal doped	Pt wire	50 % CO_2 in He	aq. KCl	CO, H_2, hydrocarbons and organics	10-20 mA	FE CO= 18.9 %; H_2= 80.6 %; hydrocarbons and organics= 0.55 %	- / 60	[76]

* Cell potential (not referred to any reference electrode)

Ampelli et al. [75] added different polymers to form Nafion-based MEAs with GDLs. Different products such as CO, CH_3OH, C_2H_5OH, C_3H_8O, acetic acid and acetaldehyde were obtained when Pt was supported on CNTs as electrocatalyst. The total *FE* was higher than 95 % in all tests. Besides, the hydrocarbon and oxygenates production for Pt-CNT with polymer (10 % weight metal) was also analysed. The results showed that doping with an active metal is not enough to increase productivity, probably due to a reduced conductivity. Nevertheless, small additions of CNT make possible to enhance the productivity to an approximate value of 7×10^{-5} mmol.

Aeshala et al. [55] also used a Nafion® membrane to produce CH_4 in a G-L ecMR. Cu was supported on carbon porous papers and a potential of 2 V was applied to the cell at ambient conditions to reach a *FE* of about 4.5 %.

Genovese et al. [76] also studied the possibility of introducing another gas (He) into the cathodic chamber together with CO_2 in a 50% concentration. A Nafion® 115 membrane was used to form a GDE with the loaded metals (Fe or Pt). In these experiments, CO, H_2, and hydrocarbons were observed, with the highest *FE* to CO achieved when the metallic Fe catalyst was used (*FE*= 18.9 %). A Pt-based catalyst was also tested but the *FE* to CO decreased. The *FE* to hydrocarbons was also less than 1 % in all cases. In this regard, Genovese et al. [17] used a MEA composed of Fe or Pt electrocatalysts supported on CNTs added to a Nafion® 117 membrane, while a Pt wire was used as counter electrode, with the aim to obtain long C-chain products. The electrolyte utilized at the anode side was a 0.5 M KCl solution. At 1 atm and 60 ^{o}C the Fe-CNTs electrocatalysts presented better performance in terms of productivity of alcohols and hydrocarbons at 2 V vs. Ag/AgCl. They concluded that both, the design of nanocarbon materials and the correct evaluation of the engineering issues of electrodes and cells are

needed steps for the development of electrochemical processes for CO_2 reduction to long-carbon chain products.

Ampelli et al. [46] used a Nafion® membrane and different metallic NP (Co, Cu, Fe and Pt) supported over a functionalized CNT, forming a GDE for its use in G-L ecMRs. In this case, CH_3OH, C_2H_5OH, C_3H_8O, acetaldehyde, acetone and some hydrocarbons (C4-C9) were observed. When CO_2 in gas phase was used at the cathode, the productivity was reduced in the following order: Fe-CNT > Fe-carbon black > Cu-CNT > Pt-CNT. The highest productivity value achieved in the system was 4.8 x 10^{-4} mmol·h^{-1} for Fe-CNT electrocatalysts. As previously mentioned, the absence of electrolyte and the higher CO_2 concentration at the catalyst surface could inhibit the mechanism of electron transfer, favouring the CO_2 dissociation to CO. Further reports from Ampelli et al. [45] demonstrated the influence of different electrocatalysts for the conversion of CO_2 to liquid fuels in gas-phase conditions using a tetrakis-phenylethene conjugated microporous polymer (TPE-CMP) doped with Pt or Fe NP. Besides, CNTs were also tested in combination with the previous catalysts with the aim to enhance productivity. A Nafion® 115 membrane was assembled with the TPE-CMP(CNTs)/GDL by hot-pressing method, forming the working electrode. The use of CNTs in combination with the electrocatalysts (30 wt% CNTs) enhanced considerably the performance due to a better dispersion of the ink onto the GDL and an enhanced electrode conductivity [45]. The best result, in terms of C1-C8 oxygenates formation, was 7.2 x 10^{-5} mmol·h^{-1}, when a 70 % Pt/TPE-CMP + 30 % CNTs was used as electrocatalyst. This may show the potential use of CMPs for the process of CO_2 reduction in ecMRs.

Cu catalysts were also studied in G-L ecMRs using a Nafion® CEM in order to obtain hydrocarbons from CO_2 [12, 52, 53]. Dewulf et al. [52] fed to the cathodic compartment

CO_2 humidified in an aqueous solution of $KHCO_3$. The obtained *FEs* ranged between 0-8 % and 0-10 % to CH_4 and C_2H_4, respectively. The highest values were achieved for a constant applied potential of -2 V.

As commented above, sandwiching the cathode, the membrane and the anode to form a MEA for CO_2 reduction in gas phase makes possible to enhance CO_2 electroreduction. In this sense, Gutiérrez-Guerra et al. [12] used a Cu powder-based MEA as cathode with a hot-pressed Sterion® membrane (CEM) and IrO_2-carbon paper as anode. Water was introduced into the anode side with N_2, while CO_2 in gas phase was used as catholyte. Besides, electrocatalytic experiments were conducted at atmospheric pressure and in a range of temperatures between 80 and 90 ^oC. CO_2 consumption rate was higher at 90 ^oC in the different supports evaluated (i.e. graphite (G), activated carbon (AG) and carbon nanofibers (CNF)). The product selectivity at the Cu-CNFs electrodes was C_2H_4O= 70 %, methyl-HCOOH= 13 %, CO= 10 %, CH_4= 7 % at -30 mA. The high selectivity for C_2H_4O can be attributed to the size of Cu particle. In addition, Cu-AC electrodes reached a selectivity of 50 % to C_2H_4O at -30 mA (with CH_3OH as the second main product). However, Cu-G electrodes led to a higher selectivity to CH_3OH (75 %) at -30 mA. As a conclusion, an increase in *CD* for Cu-G and Cu-AC electrodes led to an increase in CH_3OH selectivity due to the higher supplied rate of protons.

CH_4 and C_2H_4 were also obtained at Cu-based catalyst in a different report [77]. In this case, different anolytes were applied (KOH, $KHCO_3$, KH_2PO_4 and K_2SO_4). The results showed that the use of 1 M KOH led to the best performance when humidified CO_2 was fed to the cathode. The maximum *FE* to C_2H_4 and CH_4 were 69 % and 9.1 %, respectively, for an applied voltage of -2.72 V vs. Ag/AgCl. Conversely, Komatsu et al. [53] used a dry CO_2 gas as reactant. In this case, C_2H_4, CH_4, CO, H_2 and HCOOH were produced at 25 ^oC, although HER was predominant (*FE* about 89-97 %). They

concluded that the use of a CEM, with high protons transport capacity, is required for the production of products that need high amounts of protons and electrons such as CH_4 and C_2H_4.

Prakash et al. [56] used a gas flow electrochemical cell, in which a glass frit was used to separate the two compartments. A Sn-based cathode was applied for the production of HCOOH, with a highest performance (*FE*= 70 %) found at -1.6 V vs. NHE.

As summary, different products such as CO, HCOOH, hydrocarbons and alcohols can be achieved with high *FEs* from CO_2 electroreduction using CEM in G-L ecMRs. The use of buffer layers between cathode and membrane seems to be an interesting approach to increase the *FE* to CO and HCOOH in these reactors. Nevertheless, hydrocarbons and alcohols have been obtained with poor *FEs* (< 10 %) and productivities, except for the work developed by Cook et al. [77]. To overcome these limitations, the addition of different microporous polymers into the membrane or the utilisation of CNTs as catalytic support, among others, may be of help [45, 46]. These improvements may probably lead to a better the near future.

4.2.2. G-L ecMRs based on AEMs

Other authors have tested AEMs for CO_2 electroreduction in G-L ecMRs [11, 22, 51, 57]. Delacourt et al. [11] employed an AEM (polyethersulfone-based membrane with bicyclic ammonium groups) and humidified CO_2 as catholyte. In this case, a buffer layer ($KHCO_3$) was not included in the reactor and the *FE* to CO (3 %) was significantly lower than that obtained in configurations discussed above, in which a buffer layer and a CEM (Nafion®) were used [11]. These authors also showed that the use of AEM is advantageous when water is present at the anolyte because of the generation of $KHCO_3$. Hori et al. [51] used Ag-coated AEM as electrode. The CEM

alone was not suitable for CO_2 reduction because the surface of the membrane was partly ruptured during CO_2 reduction and the reaction was rapidly suppressed. Thus, the use of an AEM allows a sustained reduction of CO_2 to CO, HCOOH and H_2 for more than 2 h. The *FE* to CO was 92.1 % at 20 mA·cm^{-2}, whereas the *FE* to HCOOH was 12.1 % at 100 mA·cm^{-2}.

Aeshala et al. [22, 57] evaluated different membrane materials for the electrochemical reduction of CO_2 in gas phase. In the first work [22] two different types of membrane materials doped with KOH were used in order to prepare AEMs: polyethylenimine (PEI) and quaternized PEI (QPEI). Besides, polyvinyl alcohol (PVA) was used as a polymer matrix to form the membrane. The GDE was formed using Cu_2O particles supported on porous carbon papers. H_2, CO, CH_4, C_2H_4 and C_2H_6 were the main products obtained with a *FE* of 6-11 % CH_4 and 3-20 % to C_2H_6 and a product selectivity of 67.6 % for C_2H_6 and 16.4 % for CH_4. In a second work [57], the same authors evaluated a MEA configuration with CMI-7000 (CEM) and AMI-7001 (AEM) at the same conditions for humidified CO_2 electroreduction. The results showed that the performance for AMI-7001 membrane was more favourable than that for CMI-7000, since the *FE* to interesting products were 30 % to CH_4, 15 % to C_2H_5OH and 20 % to CH_3OH with AMI-7001 membrane, whereas CMI-7000 produced mainly H_2 (*FE*= 80%). That means that a correct membrane selection is essential to achieve high CO_2 electroreduction efficiencies.

In general, the use of AEMs is considerably less efficient than using CEMs for the electroreduction of CO_2 to CO (*FE*= 3 % vs. 82 %) as explained by Delacourt et al. [11], even though Hori et al. [51] obtained higher *FE* to CO (92.1 %) using a Ag-coated AEM as electrode at 20 mA·cm^{-2}. On the other hand, AEMs presented better performance than CEMs for the production of hydrocarbons since CEMs favoured HER

instead of CO_2 reduction (*FE* ~ 80 % to H_2). Therefore, future research efforts should also include the application of AEMs for the electrochemical reduction of CO_2.

4.3. Overview

Considering the crucial role of membranes in CO_2 reduction processes and the considerable amount of studies reported, an overview of the *FEs* to different products reached in the electrochemical reduction of CO_2 in L-L and G-L ecMRs at different V is carried out. Figure 9 and Figure 10 show, respectively, the *FE* as a function of the membrane applied and the main product obtained at different applied potentials vs. Ag/AgCl. It should be noted that the figures uniquely provide a picture for the comparison of different membrane materials, although the data come from studies where different variables, namely cathode materials, products, reaction medium, operating conditions and/or cell/electrode structure, may affect the results.

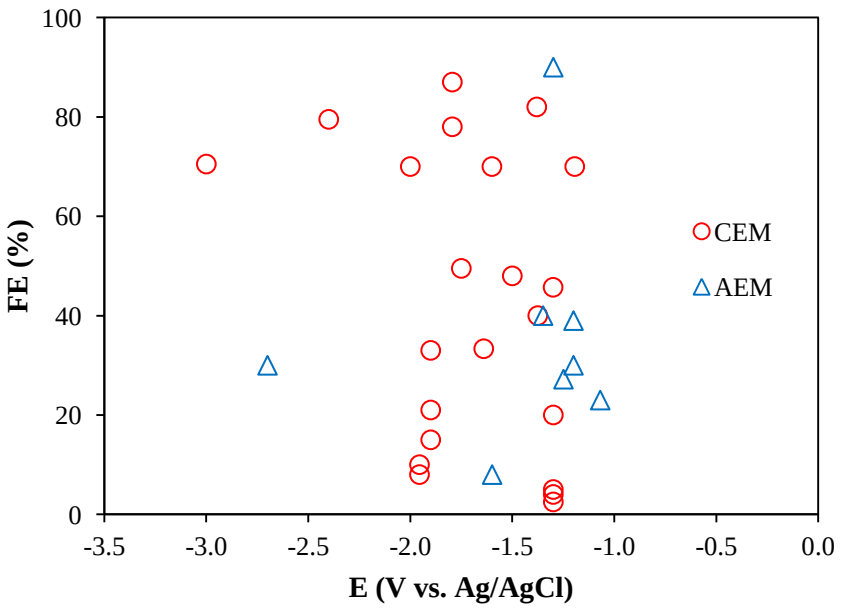


Figure 9. *FE* vs. V as a function of the type of membrane applied in L-L and G-L ecMRs.

From the figure, it seems that the use of CEMs is, in general, more favourable to reach higher *FE*s. Although it also depends on the reduced products obtained, as shown in Figure 10. Additionally, the application of CEMs are more common than AEMs for the electrochemical valorisation of CO_2, although AEMs may lower polarization losses and thus their application may be an opportunity for high efficient CO_2 electroreduction systems.

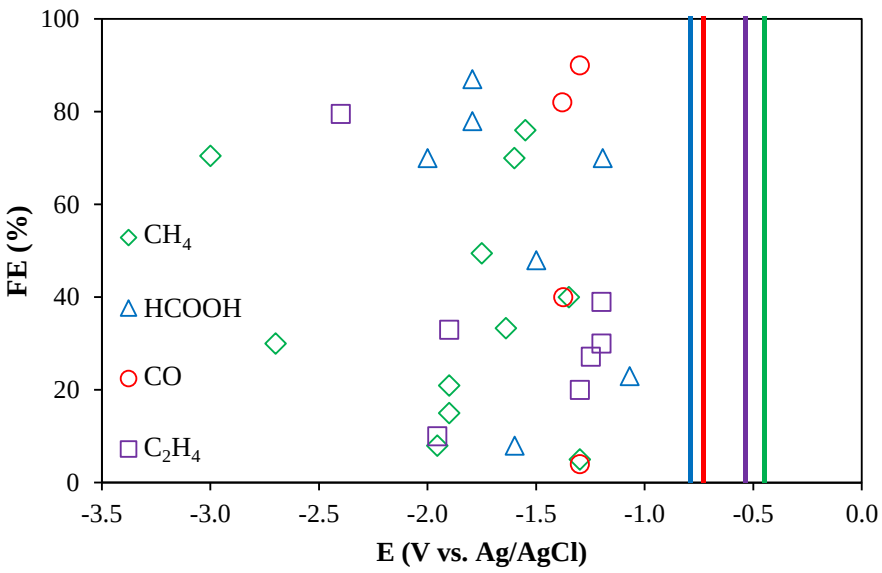


Figure 10. *FE* vs. V for the formation of main products in L-L and G-L ecMRs. The points are experimental data and the lines are referred to the equilibrium potential for each product (HCOOH= -0.809 V; CO= -0.729 V; C_2H_4= -0.539 V; CH_4= -0.439 V vs. Ag/AgCl).

Unsurprisingly, the best *FEs* were obtained for CO and HCOOH formation. The highest *FE* to CO (~ 90-100 %) was achieved using L-L ecMRs [19, 49] and a G-L ecMR [51] with Ag-based catalysts at the cathode side. Hatsukade et al. [19] achieved a *FE*= 90 % at -1.3 V vs. Ag/AgCl using a Ag-Foil as working electrode in an electrochemical reactor divided by an AEM. Besides, Rosen et al. [49] obtained a *FE* to CO near to 100

% by adding 89.5 %mol of water to the ionic liquid [bmim][BF_4] as electrolyte in a L-L ecMR divided by a CEM, where Ag NP were used as electrocatalyst. Additionally, a similar *FE* was achieved by Hori et al. [51], who reported a *FE* to CO= 92.1 % at -1.51 V vs. Ag/AgCl with a Ag-coated electrode in a G-L ecMR divided by an AEM.

On the other hand, the best *FEs* to HCOOH (~ 90 %) were achieved in L-L ecMRs with Sn-GDEs electrodes [10, 43] and CEMs at 50 $mA \cdot cm^{-2}$ and -1.8 V vs. Ag/AgCl, respectively, even though Pb plates also allowed to obtain similar *FEs* at low *CD* [20, 58]. In addition, high concentrations of HCOOH (~ 1.5 $g \cdot L^{-1}$) were achieved in Sn-GDE electrodes with smaller *FE* (70 % at -2 V and 90 $mA \cdot cm^{-2}$) by Del Castillo et al. [63].

Regarding hydrocarbon formation, the highest *FEs* to CH_4 and to C_2H_4 were 76 % at -1.55 V vs. Ag/AgCL and 79.5 % at -2.4 V vs. Ag/AgCl, respectively, in L-L ecMRs [35, 64]. In these studies, Cu-based electrocatalysts were applied in combination with CEMs in divided cells. However, other available reports did not show *FEs* higher than 50 % and 30 % in L-L and G-L ecMRs, respectively (considerably lower than *FEs* obtained to CO and HCOOH in these reactors). Therefore, the development of novel approaches in terms of reactor configuration, catalyst materials and electrolyte composition, among others, should be considered in the future in order to obtain hydrocarbons with high *FEs* and *CDs* in ecMRs.

Moreover, a deeper characterization of the reaction mechanism by which products are formed is crucial to design effective electrocatalysts for the electrochemical reduction of CO_2 [78]. Unfortunately, the different mechanisms of products obtained on different catalysts are still unclear. Different intermediates have been identified in the literature on dependence of the CO_2 reduction pathway. In this regard, $CO_2^{\cdot-}{}_{ads}$, CO_{ads}, $HCO^{\cdot}{}_{ads}$ and $H_3CO^{\cdot}{}_{ads}$ have been proposed to be probable intermediates in the electrochemical reduction of CO_2 to HCOOH, CO, CH_4 and CH_3OH, respectively. Besides, Kortlever et

al. [79] argue that the electrolyte composition and the pH may change the results of the reaction significantly. Besides, they also considered that the absorbed $CO_2^{\cdot -}$ anion intermediate and the absorbed $(CO)_2^{-}$ anionic dimer play an essential role in some of mechanistic pathways for C1 and C2 production, even though the electrocatalyst, the electrolyte and the operating conditions applied also affect in the pathways for the electrochemical reduction of CO_2. Therefore, the optimal electroreduction of CO_2 requires catalysts with suitable absorption properties and electrolytes with positive impacts on the catalytic selectivity and activity [79].

Finally, the highly endothermic CO_2 conversion reactions consume lots of energy. Therefore, the high costs associated to these processes should be considered. In this regard, the use of renewable energy might be of help in order to achieve an economically viable CO_2 electroreduction process. It seems that further efforts on evaluating the whole life cycle of CO_2 conversion processes are required.

4. Conclusions and future prospects

In this review, studies on CO_2 electroreduction in different membrane reactor configurations have been compiled and discussed in terms of type of membrane applied, electrode configuration and electrocatalyst applied in order to analyse the different technical solutions to perform the electrochemical reduction of CO_2 into valuable products using electrochemical membrane reactors. The role of membranes in these reactors is to divide the cathode and anode compartments, improving the separation of products and avoiding their re-oxidation. Besides, GDEs can be coupled with ionic exchange membranes (cation or anion) with the aim to form membrane electrode assemblies (MEAs). These systems reduce mass transfer limitations and increase

process efficiency, and are gaining importance in CO_2 electrochemical reduction processes. Nafion® membranes are the most common membranes applied, especially when high amounts of protons are necessary to form more reduced species. Liquid-Liquid electrochemical membrane cells are the most studied reactors. Gas-Gas ecMRs reports, however, are recently emerging due to the mass transport enhancements at both, cathode and anode compartments. Furthermore, different metal-based catalysts such as silver, copper, tin and lead are used as electrocatalysts for CO_2 valorisation into different products, such as carbon monoxide, hydrocarbons and formic acid, respectively in aqueous salt solutions such as Na^+, K^+, Cl^-, HCO_3^- and OH^-.

As a conclusion, further advances in new reactor configuration, membranes and catalytic materials need to be accomplished before achieving high conversion rates, *FEs* and *CDs* for the electrochemical reduction of CO_2 in ecMRs.

In this regard, the authors recommend to focus the research efforts on the:

i) development of reactor configurations based on GDEs and MEAs, which favour the transport of components; ii) addition of new polymers in ion exchange membranes, in order to improve the electrode conductivity; iii) development of new highly active nanostructured materials as catalyst support, which are able to increase the productivity for the desired products; iv) study of different electrolyte solutions, including also ionic liquids with the aim of suppressing HER; and v) identify favourable operating conditions (i.e. pressure, temperature, *V*, *CD*, and CO_2 flow rates) for an enhanced reduction of CO_2 in continuous operation.

Acknowledgements

The authors gratefully acknowledge the financial support of the Spanish Ministry of Economy and Competitiveness (MINECO) through the project CTQ2013-48280-C3-1-R. Ivan Merino-Garcia and Jonathan Albo would like to thank the MINECO for the Early Stage Researcher grant (BES2014-070081) and *Juan de la Cierva* postdoctoral program (JCI-2012-12073).

References

[1] Intergovernmental panel on climate change (2014). Climate change 2014: Mitigation of climate change. 12th session of IPPC WG III, Berlin, Germany (7-11 April 2014)

[2] J. Albo, A. Irabien, Non-dispersive absorption of CO_2 in parallel and cross-flow membrane modules using EMISE, J. Chem. Technol. Biot. 87:10 (2012) 1502-1507.

[3] G. Centi and S. Perathoner, Opportunities and prospects in the chemical recycling of carbon dioxide to fuels, Catal. Today 148 (2008) 191-205.

[4] K. S. Lackner, Carbonate chemistry for sequestering fossil carbon, Annu. Rev. Energy Environ. 27 (2002) 193-232.

[5] D. T. Whipple and P. J. A. Kenis, Prospects of CO_2 utilization via direct heterogeneous electrochemical reduction, J. Phys. Chem. Lett. 1 (2010) 3451-3458.

[6] H. R. M. Jhong, S. Ma, P. J. A. Kenis, Electrochemical conversion of CO_2 to useful chemicals: current status, remaining challenges, and future opportunities, Curr. Opin. Chem. Eng. 2 (2013) 191-199.

[7] B. Hu, C. Guild, S. L. Suib, Thermal, electrochemical, and photochemical conversion of CO_2 to fuels and value-added products, J. CO_2 Util. 1 (2013) 18-27.

[8] J. P. Jones, G. K. S. Prakash, G. A. Olah, Electrochemical CO_2 reduction: recent advances and current trends, Isr. J. Chem. 53 (2013) 1-17.

[9] E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazabal, J. Perez-Ramirez, Status and perspectives of CO_2 conversion into fuels and chemicals by catalytic, photocatalytic, and electrocatalytic processes, Energy Environ. 6 (2013) 3112-3135.

[10] D. Kopljar, A. Inan, P. Vindayer, N. Wagner, E. Klemm, Electrochemical reduction of CO_2 to formate at high current density using gas diffusion electrodes, J. Appl. Electrochem. 44 (2014) 1107-1116.

[11] C. Delacourt, P.L. Ridgway, J.B. Kerr, J. Newman, Design of an electrochemical cell making syngas (CO + H_2) from CO_2 and H2O reduction at room temperature, J. Electrochem. Soc. 155 (2008) B42-B49.

[12] N. Gutiérrez-Guerra, L. Moreno-López, J. C. Serrano-Ruiz, J. L. Valverde, A. de Lucas-Consuegra, Gas phase electrocatalytic conversion of CO_2 to syn-fuels on Cu based catalysts-electrodes, Appl. Catal. B-Environ. 188 (2016) 272-282.

[13] R. L. Cook, R. C. Macduff, A. F. Sammells, Ambient temperature gas phase CO_2 reduction to hydrocarbons at solid polymer electrolyte cells, J. Electrochem. Soc. 135 (1988) 1470-1471.

[14] S.M.A. Kriescher, K. Kugler, S.S. Hosseiny, Y. Gendel, M. Wessling, A membrane electrode assembly for the electrochemical synthesis of hydrocarbons from $CO_{2(g)}$ and $H_2O_{(g)}$, Electrochem. Commun. 50 (2015) 64-68.

[15] R. J. Lim, M. Xie, M. A. Sk, J. M. Lee, A. Fisher, X. Wang, K. H. Lim, A review on the electrochemical reduction of CO_2 in fuel cells, metal electrodes and molecular catalyst, Catal. Today 233 (2014) 169-180.

[16] Y. Oh and X. Hu, Organic molecules as mediators and catalysts for photocatalytic and electrocatalytic CO_2 reduction, Chem. Soc. Rev. 42 (2013) 2253-2261.

[17] C. Genovese, C. Ampelli, S. Perathoner, G. Centi, Electrocatalytic conversion of CO_2 to liquid fuels using nanocarbon-based electrodes, J. Energ. Chem. 22 (2013) 202-213.

[18] J. Qiao, Y. Liu, F. Hong, J. Zhang, A review of catalyst for the electroreduction of carbon dioxide to produce low-carbon fuels, Chem. Soc. Rev. 43 (2014) 631-675.

[19] T. Hatsukade, K.P Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, Insights into the electrocatalytic reduction of CO_2 on metallic silver surfaces, Phys. Chem. Chem. Phys. 16 (2014) 13814-13819.

[20] M. Alvarez-Guerra, S. Quintanilla, A. Irabien, Conversion of carbon dioxide into formate using a continuous electrochemical reduction process in a lead cathode, Chem. Eng. J. 207-208 (2012) 278-284.

[21] J. Albo, A. Sáez, J. Solla-Gullón, V. Montiel, A. Irabien, Production of methanol from CO_2 electroreduction at Cu_2O and Cu_2O/ZnO-based electrodes in aqueous solution, Appl. Catal. B-Environ. 176-177 (2015) 709-717.

[22] L. M. Aeshala, R. Uppaluri, A. Verma, Electrochemical conversion of CO_2 to fuels: tuning the reaction zone using suitable functional groups in solid polymer electrolyte, Phys. Chem. Chem. Phys. (2014). DOI: 10.1039/c0xx00000x.

[23] H. Li, C. Oloman, The electro-reduction of carbon dioxide in a continuous reactor, J. Appl. Electrochem. 35 (2005) 955-965.

[24] M. Alvarez-Guerra, A. Del Castillo, A. Irabien, Continuous electrochemical reduction of carbon dioxide into formate using a tin cathode: Comparison with lead cathode, Chem. Eng. Res. Des. 92 (2014) 692-701.

[25] P. Tamilarasan, S. Ramaprabhu, Task-specific functionalization of graphene for cathode catalyst support in carbon dioxide conversion, Journal of Materials Chemistry A (2014) 1-27.

[26] S. Kaneco, K. Iiba, S.K. Suzuki, K. Ohta, T. Mizuno, Electrochemical reduction of carbon dioxide to hydrocarbons with high Faradaic efficiency in LioH/Methanol, J. Phys. Chem. B 103 (1999) 7456-7460.

[27] K.P. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces, Energ. Environ. Sci. 5 (2012) 7050-7059.

[28] R. Kas, R. Kortlever, A. Milbrat, M. T. M. Koper, G. Mul, J. Baltrusaitis, Electrochemical CO_2 reduction on Cu_2O-derived copper nanoparticles: controlling the catalytic selectivity of hydrocarbons, Phys. Chem. Chem. Phys. 16 (2014) 12194-12201.

[29] K. J. Yim, D. K. Song, C. S. Kim, N. G. Kim, T. Iwaki, T. Ogi, K. Okuyama, S. E. Lee, T. O. Kim, Selective, high efficency reduction of CO_2 in a non-diaphragm-based electrochemical system at low applied voltage, RSC. Adv. 00 (2014) 1-3.

[30] I. Garcia-Herrero, M. Alvarez-Guerra, A. Irabien, CO_2 electro-valorisation to dimethyl carbonate from methanol using potassium methoxide and the ionic liquid [bmim][Br] in a filter-press electrochemical cell, J. Chem. Technol. Biotechnol. 90 (2015) 1433-1438.

[31] M. R. Gonçalves, A. Gomes, J. Condeço, R. Fernandes, T. Pardal, C. A. C. Sequeira, J. B. Branco, Selective electrochemical conversion of CO_2 to C2 hydrocarbons, Energ. Convers. Manage. 51 (2010) 30-32.

[32] M. R. Gonçalves, A. Gomes, J. Condeço, R. Fernandes, T. Pardal, C. A. C. Sequeira, J. B. Branco, Electrochemical conversión of CO_2 to C2 hydrocarbons using different ex situ copper electrodeposits, Electrochim. Acta 102 (2013) 388-392.

[33] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, Electrochemical reduction of CO_2 to methane at the Cu electrode in methanol with sodium supporting salts and it´s comparison with other alkaline salts, Energy & Fuels 20 (2006) 409-414.

[34] R. Aydin, H. O. Dogan, F. Köleli, Electrochemical reduction of carbon dioxide on polypyrrole coated copper electro-catalyst under ambient and high pressure in methanol, Applied Catalysis B 140-141 (2013) 478-482.

[35] H. Yano, T. Tanaka, M. Nakayama, K. Ogura, Selective electrochemical reduction of CO_2 to ethylene at a three phase interface on copper (I) halide-confined Cu-mesh electrodes in acidic solutions of potassium halides, Journal of Electroanalytical Chemistry 565 (2004) 287-293.

[36] I. Garcia-Herrero, M. Alvarez-Guerra, A. Irabien, Electrosynthesis of dimethyl carbonate from methanol and CO_2 using potassium methoxide and the ionic liquid [bmim][Br] in a filter-press cell: a study of the influence of cell configuration, J. Chem. Technol. Biotechnol. 91:2 (2016) 507-513.

[37] C. Genovese, C. Ampelli, S. Perathoner, G. Centi, Electrocatalytic conversion of CO_2 to liquid fuels using nanocarbon-based electrodes, J. Energy Chem. 22 (2013) 202-213.

[38] M. R. Singh, E. L. Clark, A. T. Bell, Effects of electrolyte, catalyst, and membrane composition and operating conditions on the performance of solar-driven electrochemical reduction of carbon dioxe, Phys. Chem. Chem. Phys. 17 (2015) 18924-18936.

[39] C. Genovese, C. Ampelli, S. Perathoner, G. Centi, A gas-phase electrochemical reactor for carbon dioxide reduction back to liquid fuels, Chem. Eng. Trans. 32 (2013) 289-294.

[40] A. Del Castillo, M. Alvarez-Guerra, A. Irabien, Continuous electroreduction of CO_2 to formate using Sn gas diffusion electrodes, AIChE J. 60 (2014) 3557-3564

[41] Q. Wang, H. Dong, H. Yu, Development of rolling tin gas diffusion electrode for carbon dioxide electrochemical reduction to produce formate in aqueous electrolyte, J. Power Sources 271 (2014) 278-284.

[42] H. Yano, F. Shirai, M. Nakayama, K. Ogura, Electrochemical reduction of CO_2 at three phase (gas/liquid/solid) and two phase (liquid/solid) interfaces on Ag electrodes, J. Electroanal. Chem. 533 (2002) 113-118.

[43] Q. Wang, H. Dong, H. Yu, H. Yu, Enhanced performance of gas diffusion electrode for electrochemical reduction of carbon dioxide to formate by adding polytetrafluoroethlyene into catalyst layer, J. Power Sources 279 (2015) 1-5.

[44] J. Albo, A. Irabien, Cu_2O-loaded gas diffusion electrodes for the continuous electrochemical reduction of CO_2 to methanol, J. Catal. (2015), http://dx.doi.org/10.1016/j.jcat.2015.11.014

[45] C. Ampelli, C. Genovese, M. Errahali, G. Gatti, L. Marchese, S. Perathoner, G. Centi, CO_2 capture and reduction to liquid fuels in a novel electrochemical setup by

using metal-doped conjugated microporous polymers, J. Appl. Electrochem. 45 (2015) 701-713.

[46] C. Ampelli, C. Genovese, B. C. Marepally, G. Papanikolaou, S. Perathoner, G. Centi, Electrocatalytic conversion of CO_2 to produce solar fuels in electrolyte or electrolyte-less configurations of PEC cells, Faraday Discuss. 00 (2015) 1-3.

[47] B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis, R. I. Masel, Ionic Liquid-mediated selective conversion of CO_2 to CO at low overpotentials, Science Express 334 (2011) 643-644.

[48] A. Salehi-Khojin, H. R. M. Jhong, B. A. Rosen, W. Zhu, S. Ma, P. J. A. Kenis, R. I. Masel, Nanoparticle silver catalyst that show enhanced activity for carbon dioxide electrolysis, J. Phys. Chem. C 117 (2013) 1627-1632.

[49] B. A. Rosen, W. Zhu, G. Kaul, A. Salehi-Khojin, R. I. Masel, Water enhancement of CO_2 conversion on silver in 1-ethyl-3-methylimidazolium tetrafluoroborate, J. Electrochem. Soc. 160 (2013) H138-H141.

[50] J. Wu, F.G. Risalvato, P.P Sharma, P.J. Pellechia, F.S. Ke, X.D. Zhou, Electrochemical reduction of carbon dioxide II. Design, assembly, and performance of low temperature full electrochemical cells, J. Electrochem. Soc. 160 (2013) F953-F957.

[51] Y. Hori, H. Ito, K. Okano, N. Nagasu, S. Sato, Silver-coated ion exchange membrane electrode applied to electrochemical reduction of carbon dioxide, Electrochim. Acta 48 (2003) 2651-2657.

[52] D. W. Dewulf, A. J. Bard, The electrochemical reduction of CO_2 to CH_4 and C_2H_4 at Cu/Nafion electrodes (solid polymer electrolyte structures), Catalysis Letters 1 (1988) 73-80.

[53] S. Komatsu, M. Tanaka, A. Okumura, A. Kungi, Preparation of Cu-solid polymer electrolyte composite electrodes and applications to gas-phase electrochemical reduction of CO_2, Electrochimica Acta 40 (1995) 745-753.

[54] C. S. Chen, A. D. Handoko, J. H. Wan, L. Ma, D. Ren, B. S. Yeo, Stable and selective electrochemical reduction of carbon dioxide to ethylene on copper mesocrystals, Catal. Sci. Technol. 5 (2014) 161-168.

[55] L. M. Aeshala, S. U. Rahman, A. Verma, Effect of solid polymer electrolyte on electrochemical reduction of CO_2, Separation and Purification Technology 94 (2012) 131-137.

[56] G. K. S. Prakash, F. A. Viva, G. A. Olah, Electrochemical reduction of CO_2 over Sn-Nafion coated electrode for a fuel-cell-like device, J. Power Sources 223 (2013) 68-73.

[57] L. M. Aeshala, R. Uppaluri, A. Verma, Effect of cation and anion solid polymer electrolyte on direct electrochemical reduction of gaseous CO_2 to fuel, Journal of CO_2 utilisation 3-4 (2013) 49-55.

[58] K. Subramanian, K. Asokan, D. Jeevarathinam, M. Chandrasekaran, Electrochemical membrane reactor for the reduction of carbon dioxide to formate, J. Appl. Electrochem. 37 (2007) 255-260.

[59] S. Singh, C. Mukherjee, A. Verma, Development of catalytic activity protocol for electrochemical reduction of carbon dioxide to value added products, Clean Techn. Environ. Policy 17 (2015) 533-540.

[60] J. Xie, Y. Huang, H. Yu, Tuning the catalytic selectivity in electrochemical CO_2 reduction on copper oxide-derived nanomaterials, Front. Environ. Sci. Eng. (2014). DOI: 10.1007/s11783-014-0742-1.

[61] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, Electrocatalytic process of CO selectivity in electrochemical reduction of CO_2 at metal electrodes in aqueous media, Electrochim. Acta 39 (1994) 1833-1839.

[62] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, Adsorption of CO accompained with simultaneous charge transfer on copper single crystal electrodes related with electrochemical reduction of CO_2 to hydrocarbons, Surface Science 335 (1995) 258-263.

[63] A. Del Castillo, M. Alvarez-Guerra, J. Solla-Gullón, A. Sáez, V. Montiel, A. Irabien, Electrocatalytic reduction of CO_2 to formate using particulate Sn electrodes: effect of metal loading and particle size, Appl. Energ. 157 (2015) 165-173.

[64] K. Manthiram, B. J. Beberwyck, A. P. Alivisatos, Enhanced electrochemical methanation of carbon dioxide with a dispersible nanoscale copper catalyst, J. Am. Chem. Soc. 136 (2014) 13319-13325.

[65] R. Kas, R. Kortlever, H. Yilmaz, M. T. M. Koper, G. Mul, Manipulating the hydrocarbon selectivity of copper nanoparticles in CO_2 electroreduction by process conditions, ChemElectroChem 2 (2015) 354-358.

[66] A. S. Varela, M. Kroschel, T. Reier, P. Strasser, Controlling the selectivity of CO_2 electroreduction on copper: the effect of the electrolyte concentration and the importance of the local pH, Catal. Today 260 (2016) 8-13.

[67] C. Genovese, C. Ampelli, B. C. Marepally, G. Papanikolaou, S. Perathoner, G. Centi, Electrocatalytic reduction of CO_2 for the production of fuels: a comparison between liquid and gas phase condition, Chem. Eng. Trans. 43 (2015) 2281-2286.

[68] C. S. Chen, J. H. Wan, B. S. Yeo, Electrochemical reduction of carbon dioxide to ethane using nanostructured Cu_2O-derived copper catalyst and palladium(II) chloride, J. Phys. Chem. C 119 (2015) 26875-26882.

[69] D. Ren, Y. Deng, A. D. Handoko, C. S. Chen, S. Malkhandi, B. S. Yeo, Selective electrochemical reduction of carbon dioxide to ethylene and ethanol on copper(I) oxide catalysts, ACS Catal. 5 (2015) 2814-2821.

[70] M. Alvarez-Guerra, J. Albo, E. Alvarez-Guerra, A. Irabien, Ionic liquids in the electrochemical valorisation of CO_2, Energy Environ. Sci. 8(2015)2574-2599.

[71] K. Ogura, M. D. Salazar-Villalpando, CO_2 electrochemical reduction via adsorbed halide anions, Energy Conservation 63 (2011) 35-38.

[72] G. Keerthiga, B. Viswanathan, R. Chetty, Electrochemical reduction of CO_2 on electrodeposited Cu electrodes crystalline phase sensitivity on selectivity, Catal. Today 245 (2015) 68-73.

[73] J. Albo, M. Alvarez-Guerra, P. Castaño, A. Irabien, Towards the electrochemical conversion of carbon dioxide into methanol, Green Chem. 17 (2015) 2304-2324.

[74] A. Dominguez-Ramos, B. Singh, X. Zhang, I.E. Hertwich, A. Irabien, Global warming footprint of the electrochemical reduction of carbon dioxide to formate, J. Clean. Prod. 148 (2015) 148-155.

[75] C. Ampelli, C. Genovese, S. Perathoner, G. Centi, M. Errahali, G. Gatti, L. Marchese, An electrochemical reactor for the CO_2 reduction in gas phase by using conductive polymer based electrocatalysts, Chem. Eng. Trans. 41 (2014) 13-18.

[76] C. Genovese, C. Ampelli, S. Perathoner, G. Centi, Electrocatalytic conversion of CO_2 on carbon nanotube-based electrodes for producing solar fuels, Journal of Catalysis 308 (2013) 237-249.

[77] R. L. Cook, R. C. Macduff, A. F. Sammells, High rate gas phase CO_2 reduction to ethylene and methane using gas diffusion electrodes, J. Electrochem. Soc. 137 (1990) 607-608.

[78] D. Ren, Y. Huang, B. S. Yeo, Electrocatalysts for the selective reduction of carbon dioxide to useful products, Chimia 69 (2015) 131-135.

[79] R. Kortlever, J. Shen, K. P. Schouten, F. Calle-Vallejo, M. T. M. Koper, Catalyst and reaction pathways for the electrochemical reduction of carbon dioxide, J. Phys. Chem. Lett. 6 (2015) 4073-4082.

Table 1

Table 1. Experimental conditions, materials, main products and significant results of the Liquid-Liquid electrochemical membrane reactors.

Ref.	T (°C)	Pressure (atm)	Membrane	Cathode	Anode	Catholyte	Anolyte	Reference electrode	Products	Main results
9	25	1	Nafion®	Ag	Pt-Ir (1:1) alloy	CO_2 , $KHCO_3$	Aq. KOH	SCE	CO, H_2	40 % FE CO at -1.42 V and 20 mA/cm^2
19	---	---	Selemion™ (anion)	Cu foil	Pt foil	CO_2 , $KHCO_3$	Aq. $KHCO_3$	Ag/AgCl (converted to RHE)	16 different products	FE: 40 % methane at -1.15 V, 25 % ethylene at -1.05 V, 23% formate at -0.87 V
20	25	1	Selemion™ (anion)	Ag foil	Pt foil	CO_2 , $KHCO_3$	Aq. $KHCO_3$	RHE	CO, H_2, formate, methane, methanol, ethanol	90 % FE CO at -1.1 V and 8% FE formate at -1.4 V
21	25	1	Nafion® 450	Mesh tinned-copper plate	platinized titanium plate	CO_2 y N2, $KHCO_3$	Aq. KOH	SHE	Formate, H_2, CO, methane	86 % FE formate at 22 mA/cm^2
22	25	1	Nafion® 117	Pb plate	DSA	CO_2 , KCl + $KHCO_3$	Aq. KOH	Ag/AgCl	Formate	14.4 mg/L and 94.7 % FE to formate at 2.5 mA/cm^2
23	25	1	Nafion® 117	Sn plate	DSA	CO_2 , KCl + $KHCO_3$	Aq. KOH	Ag/AgCl	Formate	Formate FE about 70 % at 12.25 mA/cm^2
24	25	1	Nafion® 112	Cuprous oxide films electrodeposited onto copper plates	Pt mesh	CO_2 , $KHCO_3$	Aq. $KHCO_3$	RHE	Ethane, ehylene, methane, CO	FE: 0-4 % CO, 1-5 % CH_4, 20 % C_2H_4, 2.5 % C_2H_6 at -1.1 V
25	25	1.2	Nafion® 117 or no membrane	Cu insoluble plate	Pt insoluble plate	CO_2 , NaOH or KOH in methanol	NaOH or KOH in methanol	---	Methane, H_2	Without membrane and using KOH: 35.6 % FE to methane at 0.5 V
26	---	---	Nafion® 117	Pt/Nb plate (95% Pt)	Pt/Nb plate (95% Pt)	CO_2 , methanol + [bmim][Br] + CH_3OK	Methanol + [bmim][Br] + CH_3OK	Ag/AgCl	Dimethyl carbonate	11.37 mmol/L of dimethyl carbonate
27	25	1	Cation ex. membrane	Cu mesh/modified copper electrodes	Pt mesh	CO_2 , $KHCO_3$	Aq. $KHCO_3$	Ag/AgCl	Methane, ethylene, ethane, H_2, CO	Modified electrodes: 10 % methane and 33 % ethylene at -1.9
28	25	1	Cation ex. membrane	Cu mesh/foil	Pt mesh	CO_2 , $KHCO_3$	Aq. $KHCO_3$	Ag/AgCl	Methane, ethylene, ethane, H_2, CO	Cu mesh: 15 % methane and 8 % ethylene at -1.9
29	-30	---	Nafion® 117	Cu foil	Pt foil	CO_2, sodium salts in methanol	KOH in methanol	Ag/AgCl	Methane, ethylene, formic acid, CO, H_2	70.5 % FE methane in $NaClO_4$/methanol at -3V and 22.7 mA/cm^2
30	---	1 to 60	Nafion® 117	Cu wire	Pt plate	CO_2, $LiClO_4$ in methanol	Aq. H_2SO_4	Pb(Hg)x/Pb SO4/SO42-	Methane, ethylene, CO, formic acid, acetic acid	FE At 20 bar: 25.5 % methane, 15.1 % CO, 22.1 % formic acid, 40.2 % acetic acid at -3V vs. Pb(Hg)x/$PbSO_4$/SO_4^{2-}
31	-30	---	Nafion® 117	Cu foil	Pt foil	CO_2, LiOH in methanol	KOH in methanol	Ag/AgCl	Methane, ethylene, CO, formic acid	78 % methane and ethylene at -4V

32	---	---	Selemion™ (cation)	Cu mesh/Cu-halide electrode	Pt plate	CO_2, potassium halides	Aq. potassium halides	Ag/AgCl	Methane, ethylene, ethane, CO, ethanol, H_2	FE: CuBr electrode and KBr electrolye: 5.8 % methane and 79.5 % ethylene at -2.4 V
33	---	---	FAB (anion) or no membrane	Pt/Nb plate (95% Pt)	Pt/Nb plate (95% Pt)	CO_2 , methanol + [bmim][Br] + CH_3OK	Methanol + [bmim][Br] + CH_3OK	Ag/AgCl	Dimethyl carbonate	FAB membrane: 9.74 mmol/L, undivided cell: 80.85 mmol/L
34	25	1	Nafion®	Sn-GDE	Pt plate	CO_2 , $KHCO_3$	Aq. $KHCO_3$	Hg/HgO, KHCO3	Formate, H_2, CO, methane traces	93 % FE formate at 50 mA/cm^2
35	25	1	Nafion® 117	Sn-GDE	DSA	CO_2 , KCl + $KHCO_3$	Aq. KOH	Ag/AgCl	Formate	Formate FE about 70 % and a concentration of 1348 mg/L
36	25	---	Nafion® 117	Sn-GDE	Pt foil	CO_2 , $KHCO_3$	Water	Ag/AgCl	Formate	FE 78 % formate at -1.8 V. 0.5 M $KHCO_3$ used
37	---	---	Selemion™ (cation)	Net Ag-electrode	Pt plate	CO_2 , KCl	Aq. KCl	Ag/AgCl	CO, H_2	CO conversion 100 % ($AgNO_3$ into the electrolyte). FE > 45% CO.
38	25	---	Nafion®	Sn-GDE + PTFE	Pt foil	CO_2 , $KHCO_3$	Aq. $KHCO_3$	Ag/AgCl	Formate	FE 87 % formate at -1.8 V and 22 mA/cm^2
39	25	1	Nafion®117	Cu_2O and Cu_2O/ZnO electrodes	Platinised titanium	CO_2 , $KHCO_3$	Aq. $KHCO_3$	Ag/AgCl	Methanol	FE Cu_2O: 45.7 % at -1.3 V; FE Cu_2O/ZnO: 17.7 % at -1.3 V
40	25	1	Polymer electrolyte membrane	Pt-Glassy carbon electrode	Pt wire	Deionized water or $KHCO_3$	Pure deionized water	Ag/AgCl	Formic acid	0 to 35 mM in continuous mode vs. 0 to 18 mM in discontinuous mode
41	25	---	Nafion® 117	Metal NP on carbon paper or CNT/GDL	Pt rod	CO_2 , $KHCO_3$	Aq. $KHCO_3$	Ag/AgCl	Formic acid, acetic acid, methyl formate.	2.3e-4 M formic acid (Pt-CNT), 1.8e-4 M acetic acid (Pt-CNT), 1.7e-4 M methyl formate (Cu-CB)
42	22	---	Nafion® 117	Ag - Graphite GDL	Pt black NP	CO_2, [emim][Br]	Aq. H_2SO_4	Ag/Ag+	CO, H_2	FE > 9 % CO. 90% EE at 1.5 V
43	---	---	Nafion® 212	Ag NP	Pt NP	CO_2, EMIM-BF_4	Aq. H_2SO_4	SHE	CO	Rate CO_2 conversion >> 5 nm Ag NP than Ag bulk electrode
44	---	---	Nafion® 117	Ag NP	Pt NP	CO_2, Aq. BMIM-BF_4	Aq. H_2SO_4	Ag/0.01 M Ag^+	CO	100 % FE to CO when 89.5 mol% water was added to the BMIM-BF_4
49	---	---	Selemion™ (anion)	Cu: mesocrystals or NP or electropolished	Pt mesh	CO_2 , $KHCO_3$	Aq. $KHCO_3$	Ag/AgCl	Formate, methane, ethylene, CO, H_2	Cu mesocrystals: FE: 27.2 % ethylene, 17.5 % formate, 7.5 % CO, 2.7 % methane
56	25	1	Nafion® 961 and Nafion® 430	Pb plate	IrO2/Ta2O5	CO_2 , K_2HPO_4 + H_3PO_4	Aq. KOH	---	Formate	FE 93 % formate at 2 mA/cm^2. Formate concentration increases with current density (higher value 0.01596 mol/L)
57	---	---	Nafion ®117	Cu mesh	Pt wire	CO_2, potassium halides	Aq. $KHSO_4$	Ag/AgCl	---	CD excess: KCl < KBr < KI at -1,2 V
58	25	1	Nafion®	Cu rod. Electrocatalysts: Cu, CuO, ZnO, Mo_2C, Co_3O_4	Pt/C (40% wt)	CO_2, $KHCO_3$ or KOH or DMF	Water	---	---	Cu, CuO, ZnO, Co_3O_4 actives catalysts in the protocol
59	10	---	Nafion® 112	Cu nanowires/nanonee	Pt foil	CO_2 , $KHCO_3$	Aq. $KHCO_3$	RHE	Methane, ethylene, formic acid, H_2	FE: Cu NNs: 14 % methane at -1.2V and 48 % formic acid at -0.9V; Cu NWs: 12 %

				dles						ethylene at -1.3V
60	19	---	Selemion™ (cation)	Different metal electrodes	---	CO_2, $KHCO_3$	Aq. $KHCO_3$	NHE	Methane, ethylene, CO, formate	FE in Cu electrode: 33.3 % methane and 25.5 % ethylene at -1.44V and 5 mA/cm^2
61	18	---	Cation ex. membrane	Cu single electrode/polycrystal Cu	---	CO_2, $KHCO_3$	Aq. $KHCO_3$	NHE	Methane, ethylene, CO, formate, H_2, alcohols	FE with Cu (110): 49.5 % methane y 15.1 % ethylene at -1.55V and 5 mA/cm^2

Table 2

Table 2. Experimental conditions, materials, main products and significant result of the Gas-Liquid electrochemical membrane reactors.

Ref.	T (^oC)	Pressure (atm)	Membrane	Cathode	Anode	Catholyte	Anolyte	Reference electrode	Products	Main results
9	25	1	Nafion® / anion membrane	Ag	Pt-Ir (1:1) alloy	Humidified CO_2 gas	Pure water/KH CO_3	SCE	CO, H_2	82 % FE CO with buffer layer and Nafion® membrane. 3 % FE CO with anionic membrane
41	25	---	Nafion® 117	Metal NP on carbon paper or CNT/GDL	Pt wire	CO_2 gas	Aq. KCl	Ag/AgCl	CO, H_2, methanol, acetaldehyde, ethanol, acetone, isopropanol, acetic acid.	Best productivity to products: around 4.8e-4 mmol/h on Fe-CNT
45	25	1	Nafion® with buffer layer	Sn ink + GDL	Pt/C spray + GDL	CO_2 gas	Aq. KOH	Ag/AgCl	Formate, CO, H_2	70 % FE formate at -1.2 V
46	---	1	Anion electrolyte membrane	Silver-coated	Pt plate	CO_2 gas	Aq. K_2SO_4	SHE	CO, formic acid, H_2	92.1 % FE CO at 20 mA/cm^2 and 12.1 % formic acid at 100 mA/cm^2
47	22	---	Nafion® 115	Cu foil	Pt flag	Humidified CO_2 gas	Aq. H_2SO_4	SCE	Methane, ethylene	8 % FE methane and 10 % FE ethylene at -2 V
48	25	---	Nafion®	Cu-solid polymer electrolyte	Pt mesh	CO_2 gas	Aq. K_2SO_4	SCE	Methane, ethylene, CO, H_2, formic acid	FE > 89 % hydrogen
50	25	1	Nafion®	Carbon porous	Pt/C (40 % wt Pt)	CO_2 gas	Alkali doped PVA	---	Formic acid, methanol, formaldehyde, CO, methane , H_2	4.5 % FE to methane
51	---	---	Glass frit	Sn-GDL	Pt wire	CO_2 gas	Aq. $NaHCO_3$	Ag/AgCl	Formate	FE to formate: 70 % at -1.6 V vs. NHE
52	25	1	CMI-7000 or AMI-7001	Cu_2O on porous carbon paper	Pt/C (40% wt Pt)	Humidified CO_2 gas	water	SHE	Methane, ethylene, methanol, H_2	CMI-7000: FE > 80 % H_2; AMI-7001: 30 % FE methane (2.5 V), 20 % FE methanol (2 V), 15 % FE ethylene (2 V)
53	25	1	PEI and QPEI doped with KOH (AEM)	Cu_2O on porous carbon paper	Pt/C	CO_2 gas	Deionized water	---	CO, H_2, methane, ethylene, ethane	6-11 % FE CH_4 at 2.75 V and 3-20 % FE C_2H_6 at 2.25 V
66	60	---	Nafion®	TPE-CMP doped with Pt NP	Pt wire	CO_2 gas	Aq. $KHCO_3$	---	Hydrocarbons, hydrogen, CO, methanol, ethanol, isopropanol, acetic acid, acetaldehyde	Global FE > 95 %. Hydrocarbons and oxygenates: best results with Pt doped CNT and TPE-CMP
67	60	---	Nafion® 115	GDM-metal	Pt wire	50 % CO_2 in He	Aq. KCl	Ag/AgCl	CO, H_2, hydrocarbons	18.9 % FE CO when Fe (metal doped) is used

				doped						
68	60	---	Nafion ® 115	Pt or Fe doped TPE-CMP/CNTs	Pt wire	CO_2 gas	Aq. $KHCO_3$	Ag/AgCl	C1-C8 oxygenates.	Higher productivity with 70 % Pt/TPE-CMP + 30 % CNTs (7.2e-5 mmol/h).

Figure 1

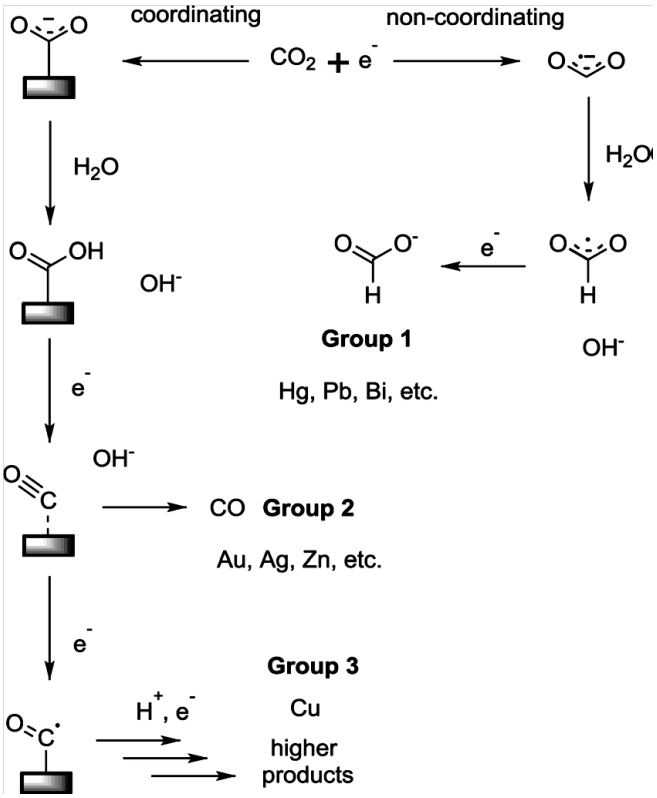

coordinating
non-coordinating
CO2 + e-
H2O
H2O
OH
OH-
e-
OH-
e-
OH-
CO
Group 1
Hg, Pb, Bi, etc.
Group 2
Au, Ag, Zn, etc.
Group 3
Cu
H+, e-
higher
products

Figure 2

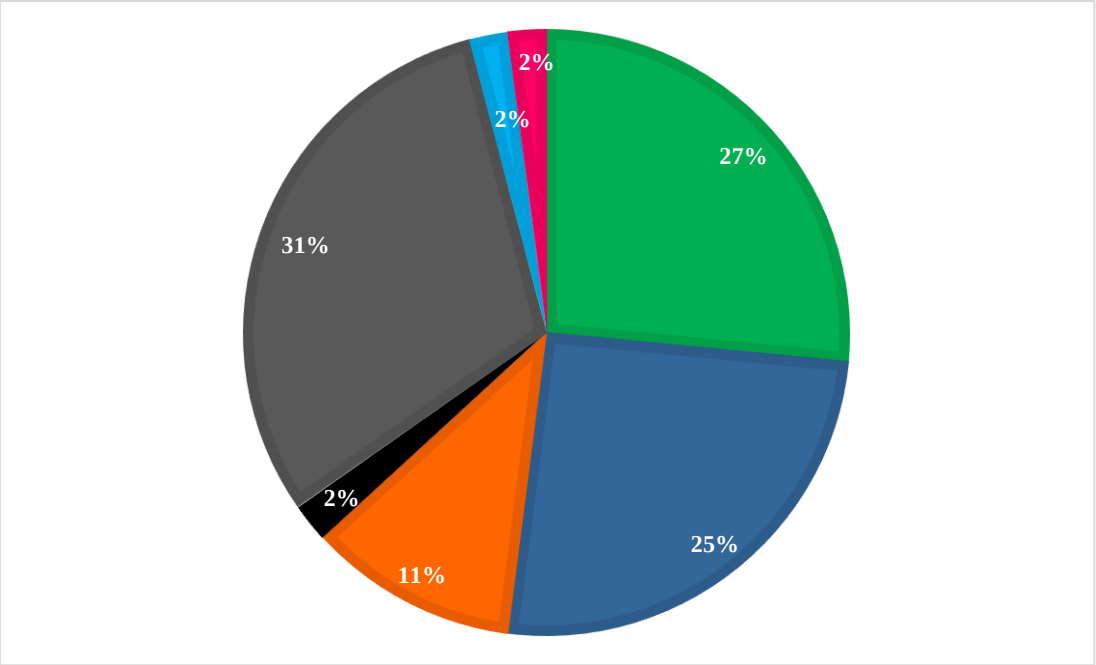


Figure 2. Distribution of the studies about ecMRs for CO_2 utilization by type of product.

Notation: formate; carbon monoxide; methane; ethylene; ethane; methanol; dimethyl carbonate.

Figure 3

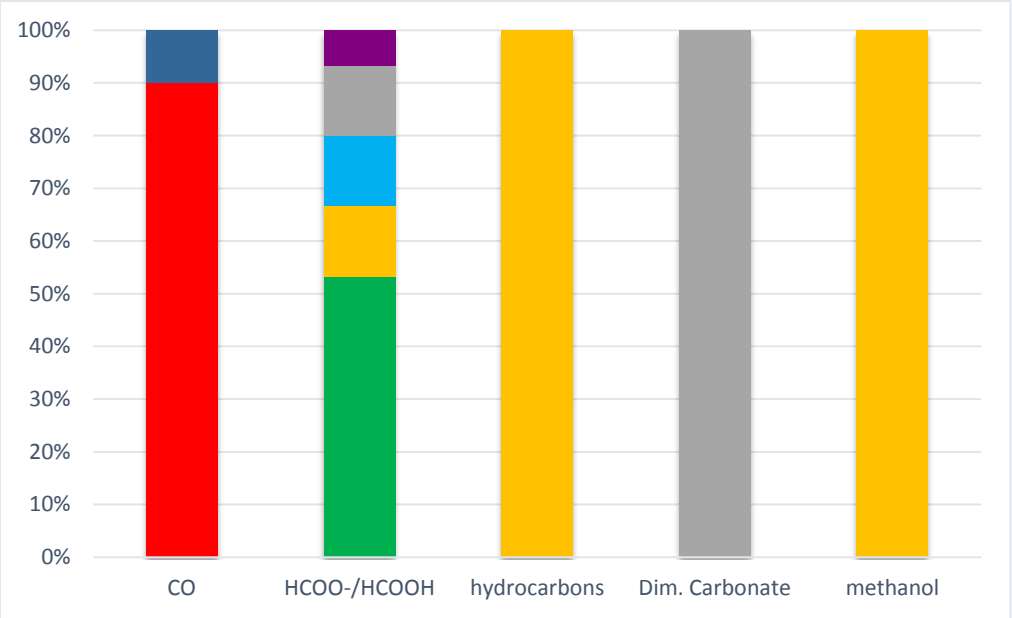

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
CO
HCOO-/HCOOH
hydrocarbons
Dim. Carbonate
methanol

Figure 4

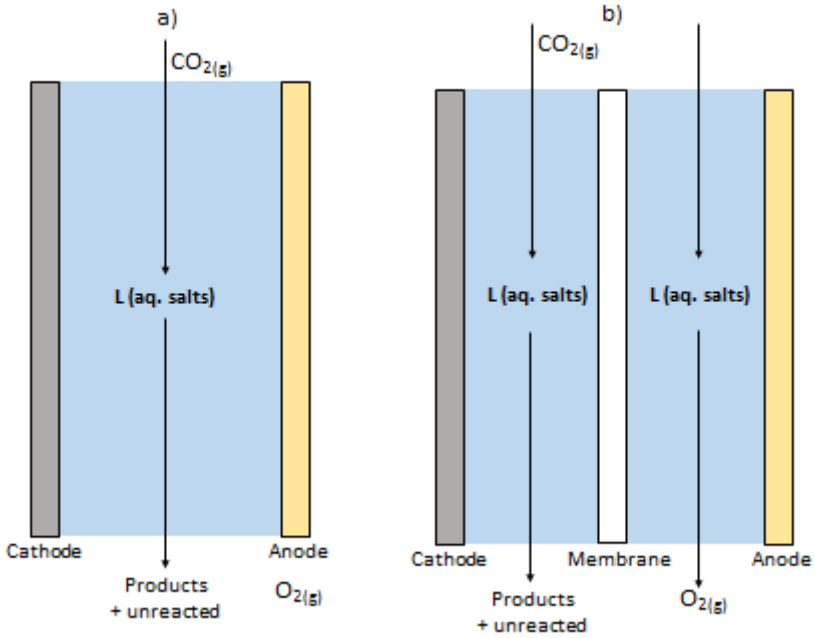


Figure 4. Conventional electrochemical reactor (a) and electrochemical reactor separated by an ion exchange membrane (b).

Figure 5

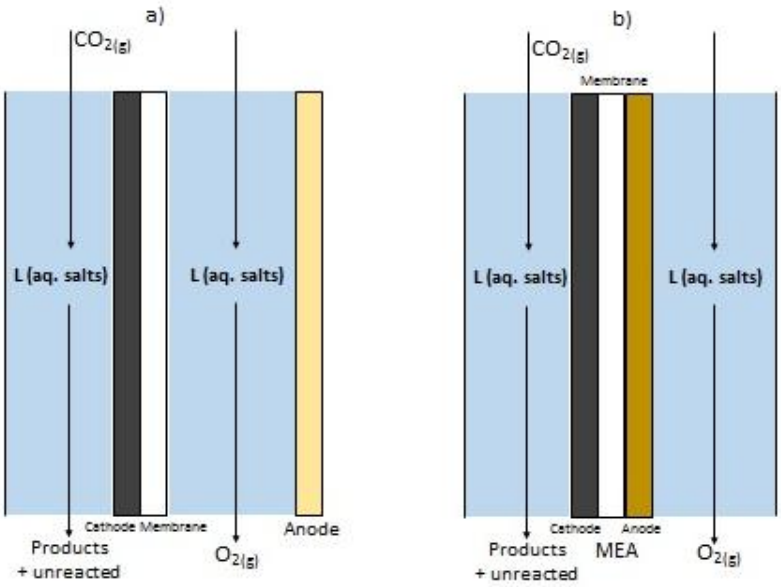


Figure 5. Catalysts dispersed at the cathode coupled with the membrane (a) and both electrodes coupled with the membrane (b).

Figure 6

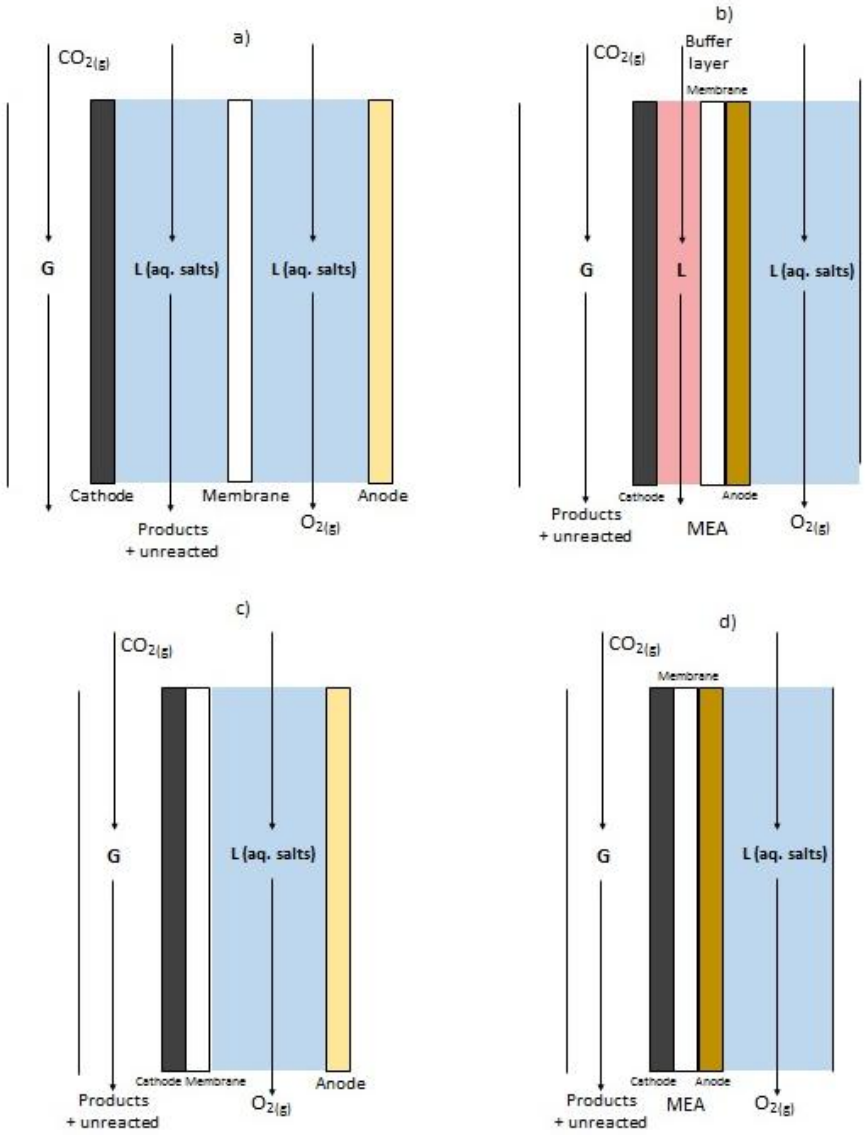

a)
$CO_{2(g)}$
G
L (aq. salts)
L (aq. salts)
Cathode
Membrane
Anode
Products
+ unreacted
$O_{2(g)}$
b)
$CO_{2(g)}$
Buffer
layer
Membrane
G
L
L (aq. salts)
Cathode
Anode
Products
+ unreacted
MEA
$O_{2(g)}$
c)
$CO_{2(g)}$
G
L (aq. salts)
Cathode Membrane
Anode
Products
+ unreacted
$O_{2(g)}$
d)
$CO_{2(g)}$
Membrane
G
L (aq. salts)
Cathode
Anode
Products
+ unreacted
MEA
$O_{2(g)}$

Figure 7

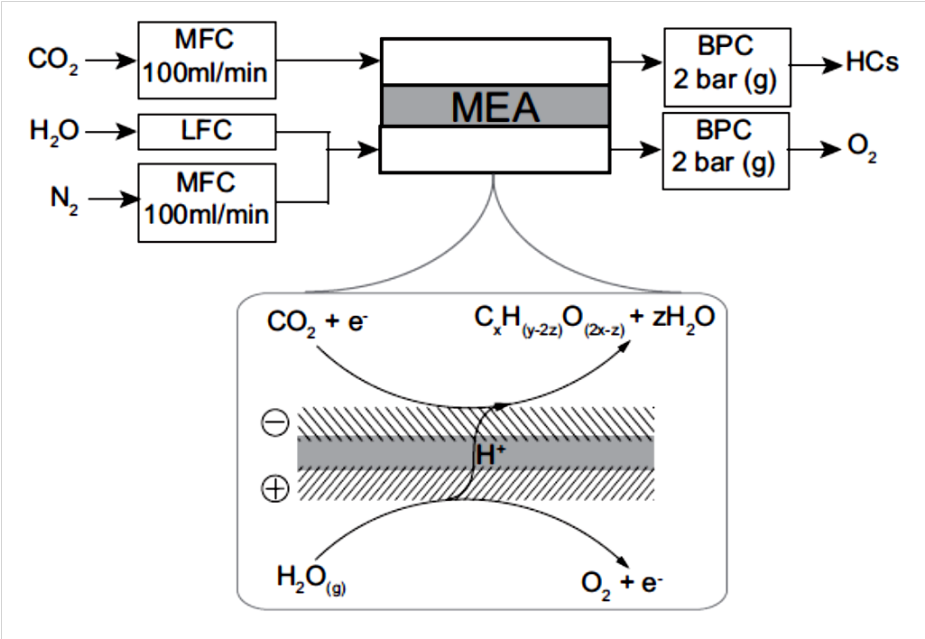


Figure 7. G-G ecMR used by Kriescher et al. [55]. Reproduced from Ref. [55].

Figure 8

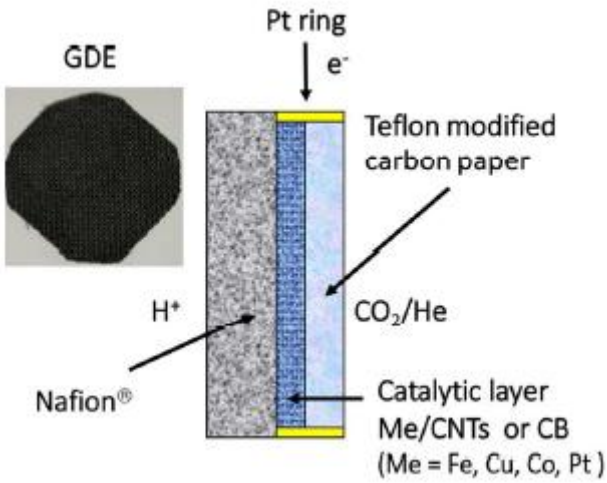


Figure 8. GDE type electrodes used for CO_2 electrochemical reduction. Reproduced from ref. [41]

Figure 9

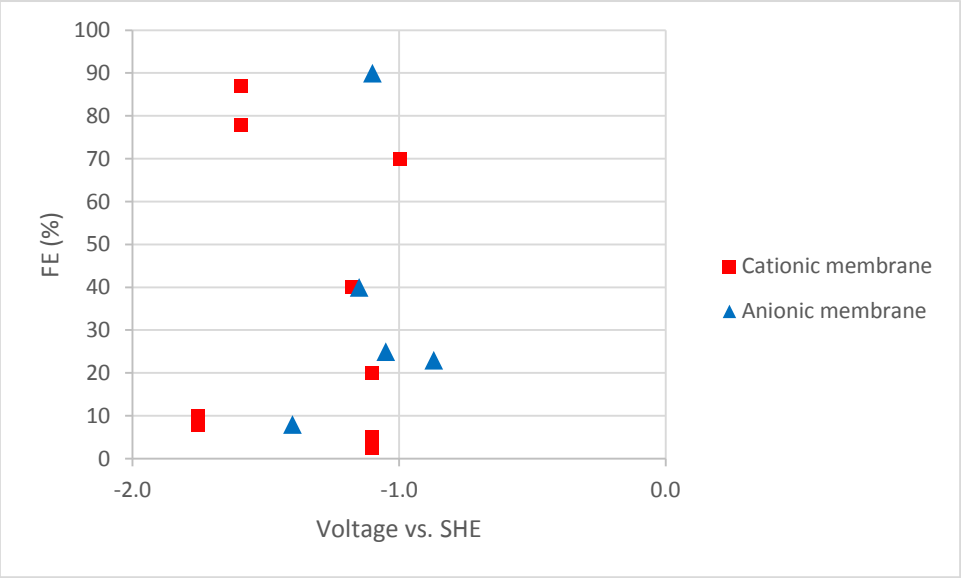
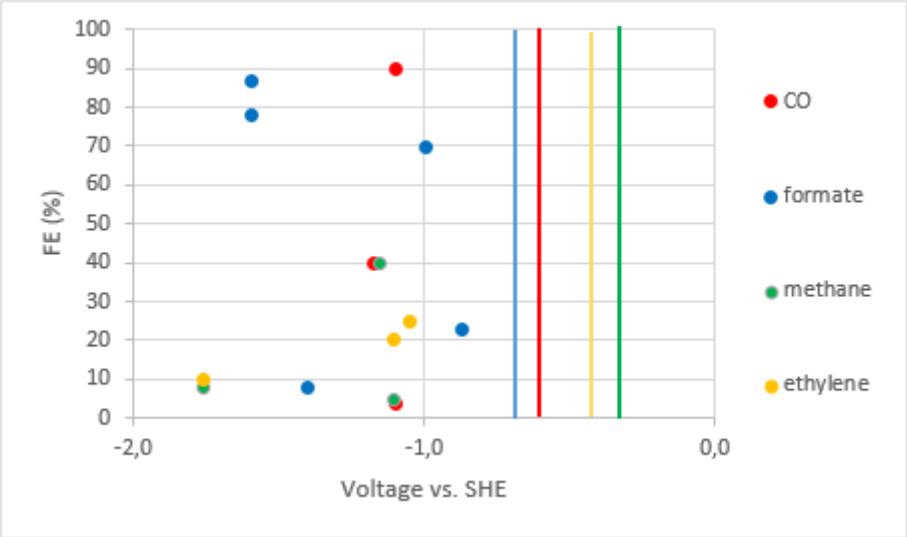

100
90
80
70
60
50
40
30
20
10
0
FE (%)
-2.0
-1.0
0.0
Voltage vs. SHE
Cationic membrane
Anionic membrane

Figure 10


100
90
80
70
60
50
40
30
20
10
0
FE (%)
-2,0
-1,0
0,0
Voltage vs. SHE
CO
formate
methane
ethylene

Captions

Figure 1. Mechanism for electrochemical CO_2 reduction on metal surfaces in water, reproduced from Ref. [7].

Figure 2. Distribution of the studies about ecMRs for CO_2 utilization by type of product. Notation: formate; carbon monoxide; methane; ethylene; ethane; methanol; dimethyl carbonate.

Figure 3. Different products as a function of the catalyst involved. Notation: Ag; Ni; Sn; Pb; Pt; Cu.

Figure 4. Conventional electrochemical reactor (a) and electrochemical reactor separated by an ion exchange membrane (b).

Figure 5. Catalysts dispersed at the cathode coupled with the membrane (a) and both electrodes coupled with the membrane (b).

Figure 6. Gas phase used at the cathode separated to the catholyte (a), gas phase at the cathode with liquid buffer layer (b), cathode coupled to membrane without buffer layer (c), and both electrodes coupled to the membrane (d).

Figure 7. G-G ecMR used by Kriescher et al. [55]. Reproduced from Ref. [55].

Figure 8. GDE type electrodes used for CO_2 electrochemical reduction. Reproduced from ref. [41]

Figure 9. FE vs. voltage as a function of the membrane type used in L-L and G-L ecMRs.

Figure 10. FE vs. voltage as a function of valuable products obtained in L-L and G-L ecMRs. The points are experimental data and the lines are referred to the equilibrium potential for each product.