

# Electrochemical Reduction of CO<sub>2</sub> on Metal Electrodes. Fundamentals and Applications Review

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Carbon dioxide can be converted to compounds such as formic acid, methanol or methane electrochemically. This electrolytic process has been proposed as a way to store energy and produce a number of compounds, most of which are currently obtained from fossil fuels. The electrochemical reduction of CO<sub>2</sub> is a challenging subject for the fundamental and applied sciences. An electrocatalyst with high activity and high selectivity is desired, therefore a good understanding of the electro reduction processes, mechanisms and kinetics, is vital. Likewise, from an engineering point of view, the cell or reactor design is also key to maximize the reduced products. In the present review the electrochemical conversion of CO<sub>2</sub> to C<sub>1</sub> and C<sub>2</sub> compounds is evaluated with emphasis in the formation of formic acid. Relevant reports are overviewed with special consideration of the works published in order to take the electroreduction process from lab to a pilot scale.

**KEYWORDS:** Electrochemical Reduction, Carbon Dioxide, Metal Electrodes, Formic Acid.

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## 1. INTRODUCTION

Carbon dioxide is a simple non-polar molecule, which is the end product of the combustion of any organic compound in the presence of oxygen and also the result of animal breathing. CO<sub>2</sub> is naturally present in the atmosphere in minor amounts (0.035%). However, since 1950 there has been an increase in the atmospheric amount of CO<sub>2</sub>, where according to the Intergovernmental Panel on Climate Change (IPCC), the CO<sub>2</sub> emission from fossil fuels has grown at a rate of 1.9% per year reaching 379 ppm in 2005 and being currently in the order of 400 ppm.<sup>1</sup>

At the same time, reserves of fossil fuels (coal, oil and gas) that are the main source for the generation of electrical energy and transportation fuel<sup>2</sup> are dwindling as they are not renewable in the human time scale.<sup>3</sup> The reduction of carbon dioxide has been envisioned as an answer to solve both issues while maintaining the atmospheric CO<sub>2</sub> amount balanced.<sup>4–8</sup> By electrochemical means, the direct products of the carbon dioxide reduction are CO, formaldehyde, formic acid, methanol, methane and oxalic acid as shown in Table I. This compounds can be used as fuels, like methanol and methane, or as precursors for building more complex molecules<sup>9</sup> ranging from ethanol and dimethyl ether (DME) to resins, olefins and gasoline, some of which today are obtained from oil.<sup>2</sup> Even though, CO<sub>2</sub> can be conveniently captured from point sources such as fossil fuel burning power plants, aluminum plants and cement industries, the source for CO<sub>2</sub> should ultimately be the atmospheric carbon dioxide<sup>10–13</sup> in order to maintain CO<sub>2</sub> levels in the atmosphere and alleviate climate change caused by human factors. In other words, the reduction of CO<sub>2</sub> is a means to store energy in the same way as hydrogen was proposed.<sup>14</sup> Electrical energy obtained from sources such hydro, wind, solar and nuclear (carbon free sources) can be used to reduce CO<sub>2</sub> to liquid fuels and then used when needed in a thermoelectric or fuel cell device to generate electricity, or in an internal combustion engine (ICE) for transportation, with the benefit of employing the same infrastructure that is currently employed for oil.<sup>4, 5, 15</sup>

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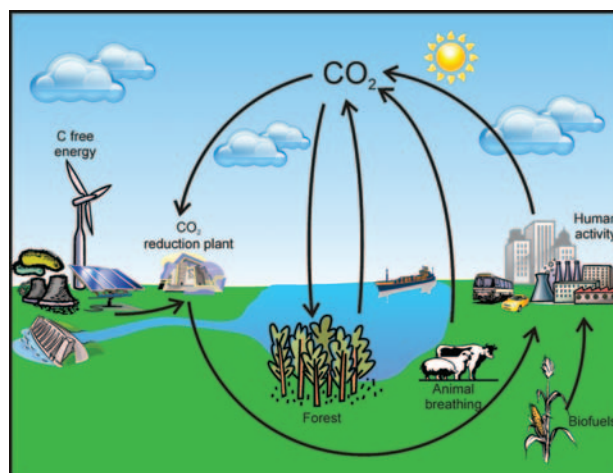
**Table I.** Standard  $\Delta G^\circ$  and corresponding  $E^\circ$  for the two-, four-, six- and eight-electron reduction of carbon dioxide in water media.

Reactions	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )	$E^\circ$ (V vs. NHE)
$\text{CO}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$	19.9	-0.103
$\text{CO}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{HCOOH}(\text{aq})$	22.1	-0.115
$\text{CO}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow \text{HCHO}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	27.5	-0.071
$\text{CO}_2(\text{g}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{CH}_3\text{OH}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	-17.3	0.030
$\text{CO}_2(\text{g}) + 8\text{H}^+(\text{aq}) + 8\text{e}^- \rightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	-130.8	0.169
$2\text{CO}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{C}_2\text{O}_4$	91.8	-0.476

Figure 1 shows a representation of the cycle described for CO<sub>2</sub> without any carbon contribution from fossil fuels. The CO<sub>2</sub> reduction plant will produce the initial building block as well as the high molecular weight compounds to be used by human activity. In the illustration are also included human and animal breathing, CO<sub>2</sub> intake and release by trees and the production of bio-fuels (wood, vegetable coal, biodiesel, etc.) from bio-mass.

The first reports for the electrochemical reduction of carbon dioxide appeared in the second half of the nineteenth century. It was demonstrated that the reduction of CO<sub>2</sub> to formic acid could be achieved on mercury or amalgam electrodes.<sup>16-21</sup> However, research on the electrochemical reduction of carbon dioxide had practically ceased after these initial reports until the oil crisis of the 70's drove a new interest on the subject, accompanied also by advances in electrochemical and spectroscopic instrumentation<sup>22-26</sup> that allowed for a better understanding of the fundamental aspects of the electrochemical reduction. In their review Jitaru and coworkers<sup>27</sup> provided the number of paper published from 1982 to 1995, which reached 59 publications in 1995. Due to the challenge the world faces in finding a long lasting solution for the energy problem it has been seen a new interest on the use of CO<sub>2</sub> as an energy carrier and carbon source<sup>28-33</sup> in the last few years.

Electrochemical processes have been present in the industry sector since electric power was available.<sup>34-36</sup> A variety of commodities like chlorine, sodium hydroxide, aluminum, oxygen and hydrogen are produced by industrial electrocatalytic processes. Other industrial examples are anodizing for corrosion protection and electroplating

**Fig. 1.** Illustrative representation of the CO<sub>2</sub> recycling process.

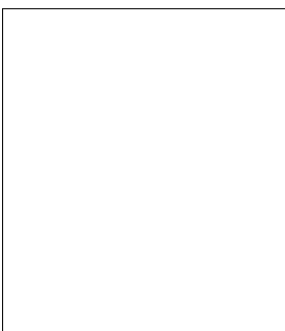
for circuit preparation in the electronic industry. Therefore, the reduction of CO<sub>2</sub> at industrial scale to produce formic acid, methanol or methane as a building block is foreseeable. However, to be economically feasible it is desirable that the processes possess current densities above 100 mA cm<sup>-2</sup> and high selectivity.<sup>37,38</sup>

This article reviews the works in the electrochemical reduction of CO<sub>2</sub> in metal electrodes, mainly for obtaining formic acid, discusses the latest works on more practical applications and evaluates balance energy aspects when the reduction products are used in fuel cells.

## 2. CARBON DIOXIDE ELECTROCHEMICAL REDUCTION REACTION MECHANISM AT METAL ELECTRODES

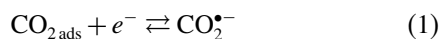
The electrochemical CO<sub>2</sub> reduction has been conducted using a wide variety of electrocatalysts, including metals,<sup>39-42</sup> non metals,<sup>43-45</sup> semiconductors,<sup>46-49</sup> coordination compounds<sup>50-56</sup> and organometallics<sup>57-60</sup> as well as employing an array of conditions such as different solvents<sup>61-66</sup> electrolytes<sup>64, 67-70</sup> and pressures.<sup>68, 71-73</sup> The different combinations of electrodes and solvents yielded a variety of products. In Table I, the products obtained from the direct reduction of carbon dioxide in aqueous media are shown.<sup>74,75</sup> The potential reduction is pH

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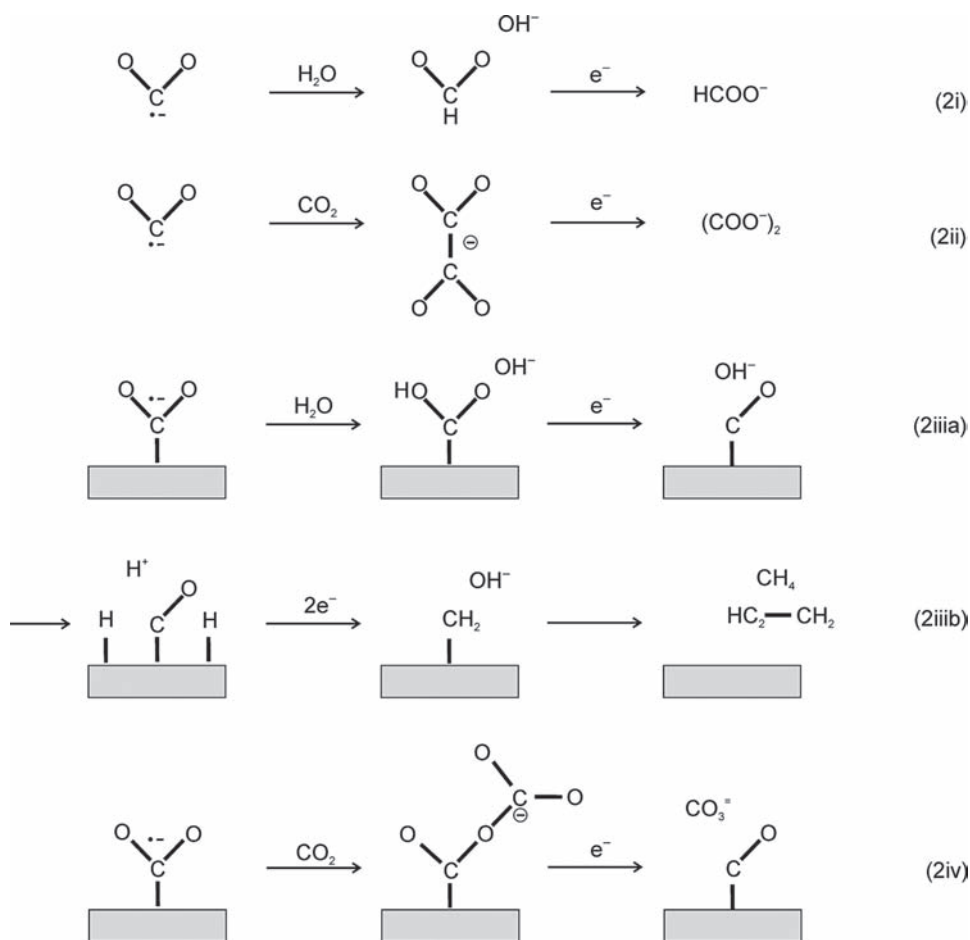
dependent and, as expected, at lower pH the processes are more favorable but at the same time the solubility of carbon dioxide decreases due to CO<sub>2</sub> equilibrium in aqueous solution,<sup>75</sup> diminishing the overall product yield. The electrolyte used in the media, particularly in water, can enhance carbon dioxide solubility. However, the electrolyte can also enhance the reduction of water (electrolysis) by the electrode (based on the pH), which competes with the carbon dioxide reduction. With the exception of the reduction to methanol and methane, all the processes are less favorable than the reduction of H<sup>+</sup> to H<sub>2</sub>. However, the difficulty of transferring multiple electrons reduces the practical feasibility to obtain such products.

The first step in the carbon dioxide electroreduction involves the formation of the CO<sub>2</sub><sup>•-</sup> radical as indicated by:<sup>27, 37, 38, 76–81</sup>



The product obtained in the CO<sub>2</sub> electrochemical reduction will then depend on the subsequent steps; whether or not the radical anion is adsorbed on the metal surface and the nature of the solvent (protic or aprotic) as presented by Hori and co-workers.<sup>82</sup> The different steps that may follow the formation of the radical anion (1) are:

The mechanism identified as (2i) involves the formation of formic acid. Such formation occurs when the radical anion is not adsorbed on the metal electrode in the aqueous media. Proton is donated from water in neutral solution while in basic solution can be also donated from the electrolyte.<sup>38, 75, 77</sup> Examples of metals promoting this pathway are; Cd, Sn, In, Tl, Hg and Pb.<sup>62, 83–88</sup> Mechanism (2ii) is analogous to (2i), but occurs in aprotic media. The radical anion can couple with itself or react with a molecule of carbon dioxide to form the oxalate di-anion. Metals that promote this mechanism include Pb, Tl, Ru and Hg.<sup>62, 84, 85, 87–91</sup> The reaction proceeds by mechanism (2iia) when the radical anion is adsorbed on the metal in aqueous media. The end product is carbon monoxide, and metals that favor this mechanism are Au, Ag and Zn.<sup>23, 87, 92–95</sup> The mechanism (2iib) is a continuation to the one identified as (2iia), with the difference that the resulting product is a mixture of hydrocarbons (methane and ethylene) and occurs when the metal electrode can also adsorb hydrogen, as is the case for Pt, Pd, Cu and Ni.<sup>27, 96–105</sup> The last pathway is mechanism (2iv), which is similar to mechanism (2ii), but since the radical anion is adsorbed on the metal electrode the coupling with another molecule of carbon dioxide proceeds through the oxygen instead of carbon, producing carbon monoxide and



eliminating the carbonate anion. Metals that facilitate this pathway are Au, Cu, Zn, Cd, Sn and In.<sup>85, 106–112</sup> The above reactions show not only the mechanism for the carbon dioxide reduction, but also reveal that the most common products for such reduction are carbon monoxide, formic acid and oxalic acid as well as methane and ethylene. Glyoxalic acid or the glyoxalate anion can be obtained by coupling two oxalates.<sup>113</sup> Products like methanol or formaldehyde are not contemplated from a mechanistic standpoint, and although their formation was reported on metals like Cu, Ag and Ru<sup>76, 77, 108, 114–118</sup> they were observed in negligible amounts. Chaplin and Wragg<sup>77</sup> also presented a comprehensive representation of the different reaction path with intermediates for the CO<sub>2</sub> electroreduction. In their review it can be observed that the products obtained for a particular metal electrode could be not as selective as it is presented in reactions shown above but a mixture of products.

### 2.1. Electrochemical Reduction to CO

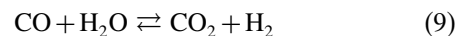
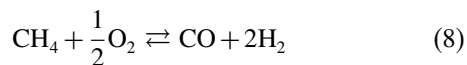
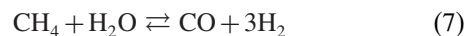
Carbon monoxide is the simplest product obtained from the electrochemical reduction of CO<sub>2</sub>. In aqueous media Au, Ag and Zn may produce CO with faradaic efficiencies in the order of 60 to 80% following pathway (2iiaa).<sup>82</sup> These *sp* metals<sup>27, 77</sup> possess high H<sub>2</sub> overpotential, ca. –2 V versus NHE, and a low H<sub>2</sub>O adsorption, allowing the radical anion to receive an electron to yield CO.<sup>93</sup> Ito et al.<sup>68</sup> obtained CO, H<sub>2</sub> and HCOO<sup>–</sup> on Au electrodes. Between –1.3 to –1.6 V versus SCE, only CO and H<sub>2</sub> were formed. Hori and coworkers<sup>93</sup> observed the formation of HCOO<sup>–</sup>, CO, CH<sub>3</sub>OH, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> at Au, Ag and Cu. At potentials below –1.4 V versus SCE, CO was exclusively formed.

In non aqueous media the faradaic efficiency is also high, close to 80%, in Au, Cu, Zn, Cd, Sn and In following pathway (2iv),<sup>27, 77, 82</sup> which is a reductive disproportionation of CO<sub>2</sub>, with the formation of CO and carbonate ions.<sup>63, 119</sup> The metals for pathways (2iv) Cd, Sn and In have a higher H<sub>2</sub>O adsorption than Au, Ag and Zn and therefore these metals produce mainly formic acid in aqueous media (*vide infra*).<sup>27, 28, 77</sup>

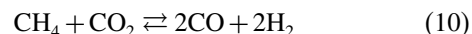
The metals identified as *d* metals i.e., Pt, Pd, Cu and Ni lead to the formation of methane and ethylene in aqueous media according to pathway (2iiib), however, actual experiments have shown the formation of CO in high yield, 70 to 80%, and a mixture of compounds including methanol.<sup>24, 38, 97, 100, 108, 120</sup> Noda et al.<sup>99</sup> evidenced the presence of CO, ethane and methane on Cu electrodes. Jitaru reported that these *d* metals produced preferably CO in non aqueous media.<sup>28</sup>

Carbon monoxide as a product must not be underestimated. CO and H<sub>2</sub> are the components of synthesis gas or syngas used in the Fisher–Tropsch (FT) process to produce synthetic liquid oils and solvents.<sup>5, 121–124</sup> The syngas is a mixture of CO, H<sub>2</sub> and CO<sub>2</sub> of various compositions, which nowadays is obtained from fossil fuels; gas, coal

and oil.<sup>121–123</sup> In the presence of water or O<sub>2</sub> through steam reforming (7), partial oxidation (8) and water gas shift (WGS) (9) reactions, exemplified below for methane, the fossil fuels produces mixture of CO, H<sub>2</sub> and CO<sub>2</sub> in the desired proportion:



Another common reaction is the dry reforming (10) by which methane is mixed with CO<sub>2</sub> to obtain CO and H<sub>2</sub>.

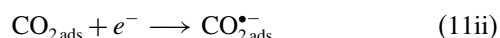


The syngas mixture is then reacted in a heterogeneous reaction over copper based catalyst to produce hydrocarbons.<sup>124</sup> For example, nowadays methanol is produced almost exclusively by a FT process from syngas.<sup>5</sup>

As described in Section 2, the products from the electroreduction of CO<sub>2</sub> are generally a mixture of compounds. In aqueous media H<sub>2</sub> is always present, and the H<sup>+</sup> reduction reaction is the main competition for the CO<sub>2</sub> electroreduction.<sup>28</sup> In the particular case of the electroreduction to CO, this has been used as an advantage and researchers have worked intensively in adjusting the electroreduction condition in order to obtain a CO/H<sub>2</sub> mixture that can be used directly in the FT process.<sup>125, 126</sup>

### 2.2. Electrochemical Reduction to Formic Acid

The complete proposed mechanism for the reduction of CO<sub>2</sub> to formic acid proceeds according the following equations:<sup>27, 78, 83, 127</sup>



The first step is the adsorption of carbon dioxide over the electrode. This step (11i) is generally disregarded in electrochemical kinetics, however, in order to have the reaction occurring, carbon dioxide must first dissolve in the media so it can be situated near or in contact with the electrode, i.e., in the adsorbed state. Therefore, the media and the electrolyte play significant roles. Table II shows the solubility of carbon dioxide in different solvents. In water, carbon dioxide has a low solubility, particularly at acidic pH. At neutral to basic pH, the solubility is slightly increased by the formation of bicarbonate, which can revert to carbon dioxide. On the other hand, in organic solvents the solubility of carbon dioxide is higher than in water, as observed in Table II, and therefore several organic solvents have been employed in the CO<sub>2</sub> electroreduction.<sup>27, 28, 77</sup>

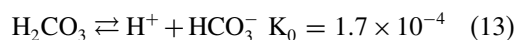
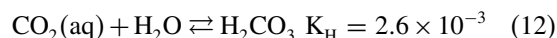
**Table II.** Carbon dioxide solubility in different solvents at 298 K and 1 atm.<sup>128</sup>

Solvent	Solubility (M)
Water	0.033
Propylene carbonate	0.14
Acetonitrile	0.28
Dimethylsulfoxide	0.135
<i>N,N</i> -dimethylformamide	0.175
Tetrahydrofuran	0.211

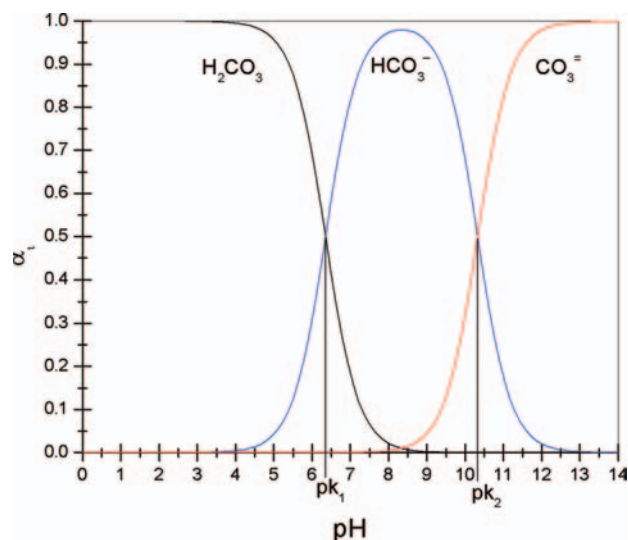
In step (11ii) of the mechanism, the adsorbed carbon dioxide is reduced to the radical anion. In the mechanism presented by Hori,<sup>82</sup> reaction (2ii) in Section 2, the radical anion that is not adsorbed on the electrode gets protonated to an HCOO<sup>•</sup> radical, which is then further reduced to formic acid. However, other authors<sup>27,38</sup> have proposed that the radical anion formed stays in the adsorbed state. The standard potential for the whole process shown in Table I, is  $-0.115$  V against the NHE. Although negative, the potential is low and it would be expected that the reduction would be facile. However, the standard reduction potential for the step (11ii) of the above mechanism has been estimated to be  $-1.66$  V versus NHE.<sup>76,129</sup> This value is the source of the high overpotential required for the reduction of carbon dioxide in water. It has been reported that the potential must be below  $-1.4$  V versus NHE for the reaction to begin.<sup>107</sup> This overpotential was also related to the energy necessary to break the linearity of the carbon dioxide molecule.<sup>75</sup> In fact faradaic yields above 90% for the electroreduction of carbon dioxide to formic acid were observed at potentials of ca.  $-1.6$  V versus NHE.<sup>82,85,88,130</sup> This large overpotential also plays a role in the adsorption of the radical anion intermediate. The metal electrode's point of zero charge (PZC) will provide the environment for the radical anion to be adsorbed.<sup>131</sup> The PZC is the electrode potential value at which the charge of the electrode surface and the related interfacial potential are zero. At potentials more positive than the PZC, the electrode surface is positively charged and at potentials below the PZC the electrode surface is negatively charged.<sup>132</sup> In terms of the carbon dioxide electroreduction mechanism, metals with highly negative PZC will provide better conditions for the adsorption of the radical anion and the subsequent protonation. On the other hand, the HCOO<sup>•</sup> radical, once formed, will stay adsorbed because of the unpaired electron until it becomes reduced to formate.

Carbonate and bicarbonate solutions have proved to be good electrolytes for the carbon dioxide electroreduction from the pH standpoint.<sup>82–85,88,94,133</sup> Bicarbonate solutions with concentrations ranging from 0.1 M to 0.5 M, the most commonly used concentrations, would give a pH of ca. 8.0 at which the CO<sub>2</sub> is in the form of bicarbonate (HCO<sub>3</sub><sup>-</sup>) increasing slightly the gas solubility in water.<sup>75</sup> Figure 2 shows the predominance of the different carbonic species at different pH in aqueous media ( $\alpha$  plot), which

is obtained from the equilibrium reactions (14) and (15). The value of the equilibrium constant for reaction (14) is the product between  $K_H$  and  $K_0$  and represents the equilibrium between CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> in a more accurate way than Eq. (13), since less than 1% of the dissolved CO<sub>2</sub> is present as H<sub>2</sub>CO<sub>3</sub>.



The best electrocatalytic metals for the electrochemical reduction of carbon dioxide to formic acid were found to be In, Pb and Sn. They present high hydrogen overpotentials (ca.  $-2.0$  V vs. NHE), which assure a low competing reaction, and a low PZC. The electrochemical measurements performed on these metals have provided some kinetic information. The Tafel plots obtained from polarization and linear sweep voltammetry yielded two linear regions for various metals<sup>38</sup> indicating two consecutive steps in the reduction process in agreement with the reaction mechanism (11). Vassiliev and co workers<sup>38</sup> obtained values between 80 to 120 mV for the first region of the Tafel slope, whereas the second region of the slope was between 300 to 400 mV, which agrees with results obtained by other authors.<sup>39,83,133,134</sup> Experiments employing different pressures of carbon dioxide demonstrated that there was no effect on the first region, indicating zero order, while an order of one was found for the second region.<sup>127,134</sup> The reaction rate dependence with the pH was also studied and found to be virtually independent,<sup>37,83</sup> except that at high pH the reaction rates are slightly diminished due to the formation of HCO<sub>3</sub><sup>-</sup> with the subsequent



**Fig. 2.** Distribution species diagram ( $\alpha$  plot) for carbonic acid (H<sub>2</sub>CO<sub>3</sub>).  $\alpha_i$  stands for the molar fraction of species  $i$ .

decrease of free carbon dioxide. However, there seems to be no clear agreement on which of the two electrons transfer is the rate determining step (rds). Kapusta and co-workers<sup>83</sup> assigned the first electron transfer (11ii) as the rds assuming Langmuir conditions for In electrodes as they observed only one Tafels slope of 115 mV. While the change in Tafel slope for electrodes like Sn was considered as a change in the rds. They also presented a two step mechanism in which steps (11iii) and (11iv) are combined. On the other hand, in an older report by Eyring and coworkers,<sup>127, 135</sup> the rds was assigned at the more positive potential region to the second electron transfer (11iv) because they observed an accumulation of the radical intermediate, while the first electron transfer (11ii) was considered to be the rds in the region of more negative potential. They also proposed a two step mechanism in a later work where steps (11ii) and (11iii) were combined.<sup>134</sup>

Formic acid is a valuable compound as itself and as a precursor. The formic acid is a liquid at ambient temperature, is a good candidate as a fuel for Direct Formic Acid Fuel Cells (DFAFC)<sup>136, 137</sup> and recently has been proposed as an optimal hydrogen carrier.<sup>52, 138, 139</sup> Global production of formic acid was 498,000 T in 2007<sup>140</sup> reaching 720,000 T in 2009.<sup>141</sup> Formic acid is used in the leather and rubber industry,<sup>142</sup> it is recognized by the U.S. Food and Drug Administration (FDA) as a safe food additive<sup>143, 144</sup> and is used as a preservative food industry for livestock.<sup>142</sup> As a precursor, formic acid can be reacted with methanol to form methyl formate which by catalytic hydrogenation produces two molecules of methanol:



Reaction of formic acid with formaldehyde also produces methanol with evolution of CO<sub>2</sub>:



These are the first steps in the use of formic acid as a precursor, from methanol the process can continue to ethylene, propylene, light olefin, alkanes and so on.<sup>5</sup>

### 2.3. Electrochemical Reduction to Methane, Methanol and Others

Of the different products obtained from the electroreduction of CO<sub>2</sub>, methane and methanol will be the more readily useful as they are used currently as fuels and chemical precursors.<sup>5, 145</sup> The mechanisms proposed by Hori<sup>82</sup> and discussed in Section 2 show that Pt, Pd, Ni and Cu promote the formation of methane and hydrocarbons as shown in (2iib).<sup>146–148</sup> Nevertheless, reports have shown the formation of mixtures of formaldehyde, ethanol and propanol among others in Cu electrodes.<sup>77, 149</sup> Other reports have shown the formation of only CH<sub>4</sub> and ethylene under

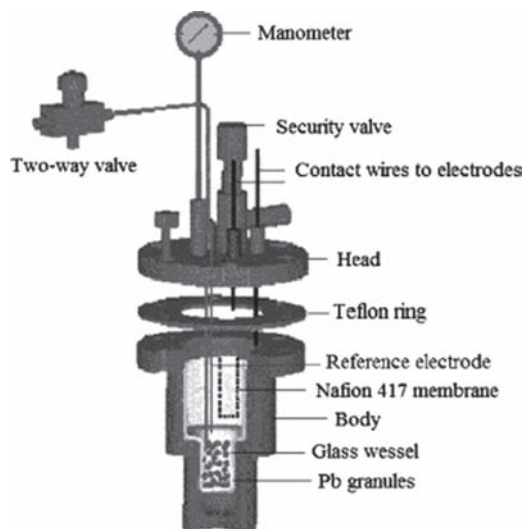
various conditions.<sup>69, 100, 109, 150, 151</sup> Komatsu et al. obtained ethylene as main product, besides H<sub>2</sub>, with faradaic efficiency between 3 to 9% in Cu based electrode<sup>152</sup> at –1.5 V versus SCE with a total current density of ca. 25 mA cm<sup>-2</sup>. Yano et al.<sup>100</sup> reported CO, CH<sub>4</sub> and ethylene in net Cu electrodes. They perform the electroreduction at potentials between –0.6 to –2.2 V versus Ag/AgCl obtaining ca. 10% as the best faradaic efficiency for methane and 40% for ethylene with no report of the current densities. Nonetheless, in Cu electrodes a deactivation of the electrode due to the formation of strongly adsorbed species was observed<sup>153</sup> stopping the electroreduction of CO<sub>2</sub> after short periods of time. All, Pt, Pd and Ni have shown strong adsorption of CO<sub>2</sub>,<sup>77</sup> therefore exhibiting desirable electrocatalytic properties for CO<sub>2</sub> electroreduction. However, H<sub>2</sub> adsorption is also high, competing with CO<sub>2</sub> at ambient pressure. Reports on Pd showed the formation of mixtures of formaldehyde, formic acid, methanol and hydrocarbons in low faradaic yields (< 10%).<sup>27, 85, 119</sup> In Ni electrodes Jitaru et al.<sup>27</sup> indicated the formation of mixtures of CO, ethanol and hydrocarbons with faradaic yields below 5%. In non aqueous media, solubility of CO<sub>2</sub> is higher than in water as was mentioned in Section 2. In methanol media, Cu electrodes produced CH<sub>4</sub> with moderate yields (~ 40%).<sup>27</sup> Several authors observed only CH<sub>4</sub> and ethylene in different non aqueous media<sup>154–157</sup> with faradaic efficiencies in the order of 10% for ethylene and below 5% for methane.

Methanol and methane not only can be used as a precursor for high molecular weight compounds, but they are also currently used as fuels. Methane is employed as natural gas and compressed natural gas (CNG) for home and transportation application, while methanol is used as a fuel in ICE and in direct methanol fuel cell (DMFC). Nevertheless, based on the low faradaic efficiencies for both compounds, typically below 10%, and low selectivity for the metal catalyst, methane or methanol does not appear to be the most convenient species for the direct electroreduction of CO<sub>2</sub>.

## 3. ELECTROCHEMICAL CO<sub>2</sub> REDUCTION CELL AND DEVICES

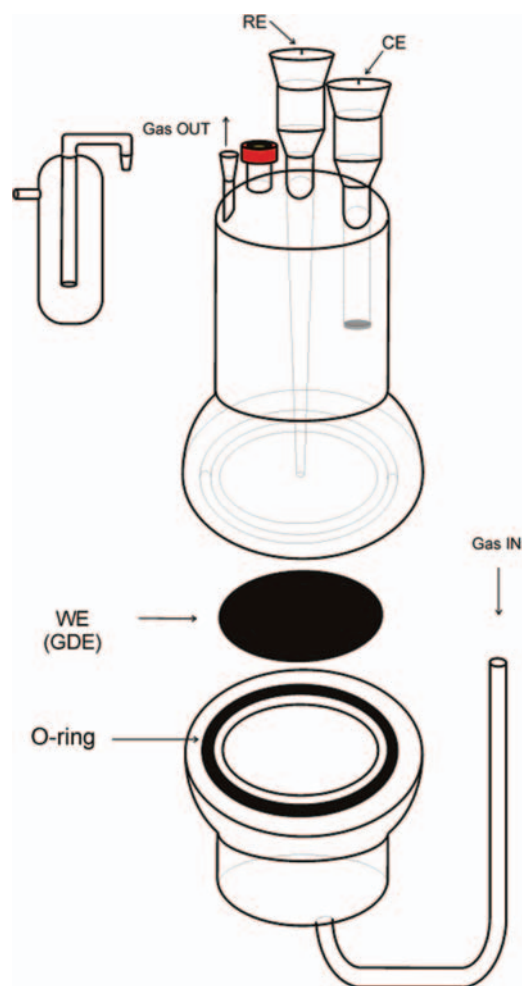
The vast majority of the CO<sub>2</sub> electrochemical reduction research was conducted at lab scale in three electrodes electrochemical cells. Recently a number of researchers have started to assemble a demonstration cell in order to scale up the process. The main research focus in this area was the increase of the surface area electrodes<sup>92, 130, 158–160</sup> mainly for the production of formic acid, due to the high faradaic efficiency observed on Pb, Sn and In (*vide supra*). In that direction, several authors worked on electrodes taking as a model the gas diffusion electrodes (GDE) used in fuel cells.<sup>152, 161–165</sup> In some cases, membrane cells or fuel cell type of cells have been assembled.<sup>162, 166, 167</sup>

Mahmood et al.<sup>168, 169</sup> were among the first researchers to use a GDE for the electroreduction of CO<sub>2</sub>. In their first work they use In, Sn and Pd impregnated GDEs and in a follow up work, metal phthalocyanine impregnated GDE. With Pb based GDE they reported formic acid formation with faradaic efficiencies of ca. 100% and current densities above 100 mA cm<sup>-2</sup> at potentials of -1.8 V versus SCE. Todoroki et al.<sup>170</sup> reported the formation of formic acid with a current density of 560 mA cm<sup>-2</sup> in In electrodes under 60 atm pressure in KHCO<sub>3</sub> at potentials ca. -1.2 V versus Ag/AgCl. Furuya et al.<sup>171</sup> prepared a cell with Pd and Pt GDE electrodes where the main products were CO and formic acid. H<sub>2</sub> was supplied to the Pt electrode and CO<sub>2</sub> to the Pd electrode with aqueous carbonate as electrolyte. Furuya et al.<sup>172</sup> reported formic acid with 90% efficiency and current densities of 80 mA cm<sup>-2</sup> at -1.1 V versus NHE in RuPd GDE electrodes. Hara and coworkers<sup>102, 158</sup> used Pt based GDE in a reactor under different pressures, from 1 to 50 atm, and obtained methane with faradaic efficiencies between 30 to 40% at ca. -1.9 V versus NHE. In the product mixture ethanol, ethylene, ethane, carbon monoxide, and formic acid were also obtained. Koleli and coworkers<sup>88, 130, 159</sup> presented a series of works where they used a pressurized bed reactor with Pb and Sn for the formation of formic acid. They obtained formic acid with 94% faradaic efficiency at -1.8 V versus SCE and 0.7 mA cm<sup>-2</sup> in 0.2 M K<sub>2</sub>CO<sub>3</sub>.<sup>159</sup> Figure 3 shows a schematic representation of their pressure reactor. Prakash et al.<sup>165</sup> prepared Sn-Nafion GDE for the reduction of CO<sub>2</sub> to formic acid in 0.5 M NaHCO<sub>3</sub>. The faradaic efficiency obtained reached 70% with a current density of 27 mA cm<sup>-2</sup>, one of the highest reported, at -1.6 V versus NHE under ambient pressure conditions. Figure 4 shows a schematic of the glass

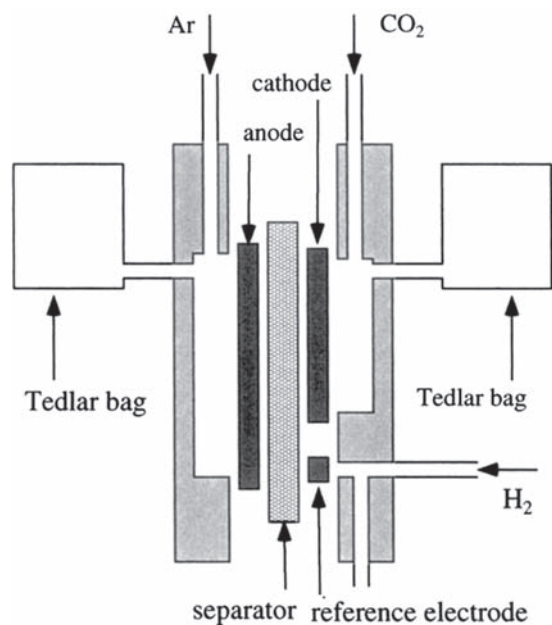


**Fig. 3.** Schematic representation of the fixed bed reactor used by Koleli et al. Reproduced with permission from [159]. F. Köleli and D. Balun, *Appl. Cat. A* 274, 237 (2004), © 2004.

cell used. Yamamoto et al.<sup>161</sup> produced syngas with a 1:1 CO/H<sub>2</sub> (v/v) gas ratio in a fuel cell-like-device using Ni as catalyst. They obtained an overall efficiency of ca. 45% at cell voltage of 3.05 V with a current density of 10 mA cm<sup>-2</sup>. In Figure 5 a diagram of the cell arrangement used is shown. Li and Oloman<sup>162, 173, 174</sup> reduced CO<sub>2</sub> in a continuous reactor with a fuel cell like arrangement. The initial design used a tinned-copper cathode where they obtained a faradaic efficiency of 86% for formate<sup>162</sup> at cell voltages between 3 to 6 V and current densities ranging from 20 to 200 mA cm<sup>-2</sup>. The following design<sup>174</sup> used only Sn as electrocatalyst with which they obtained faradaic efficiencies for formate between 63–91% at cell voltages between 2.7 to 4.3 V and current densities ranging from 60 to 310 mA cm<sup>-2</sup>. Machunda et al.<sup>164</sup> reported the results for a zero gap cell with Sn based GDE obtaining 70% faradaic efficiency at -1.6 V versus NHE for formic acid but with an average current density of 2 mA cm<sup>-2</sup>. Narayan et al.<sup>166</sup> assembled a fuel cell-type device for



**Fig. 4.** Ambient pressure glass cell used for by Prakash et al. WE: Working electrode. RE: Reference electrode. CE: Counter electrode. Reproduced with permission from [165]. G. K. S. Prakash, et al., *J. Power Sources* 223, 68 (2013), © 2013.



**Fig. 5.** Schematic diagram of the fuel cell arrangement used by Yamamoto et al. Reproduced with permission from [161], T. Yamamoto, et al., *Electrochim. Acta* 47, 3327 (2002), © 2002.

the electroreduction of CO<sub>2</sub> using Pb as electrocatalyst in basic media. Reduction experiments were conducted galvanostatically applying 40 mA cm<sup>-2</sup> at different time periods. Initial faradaic efficiencies were ca. 80%, however, they observed a decrease in the efficiency over the run periods due to diffusion barriers of the bicarbonate ion and the CO<sub>2</sub> at the electrode surface resulting in efficiencies values of 45–50%.

In an effort to scale-up the electroreduction, researchers at Det Norske Veritas (DNV), focusing on the process



**Fig. 6.** DNV demonstration reactor assembled in a solar-powered trailer. Reproduced with permission from [167], N. Sridhar and D. Hill, Carbon Dioxide Utilization, Electrochemical Conversion of CO<sub>2</sub>—Opportunities and Challenges (2011), Position Paper 07, © 2011, Det Norske Veritas.

that they call Electrochemical Reduction of CO<sub>2</sub> to Formate/Formic Acid (ECFORM), assembled a demonstration semi-pilot size reactor with a 600 cm<sup>2</sup> surface area and the capacity of reducing approximately 1 kg per day of CO<sub>2</sub> powered by photovoltaics in a movable trailer.<sup>167</sup> The device used electrodeposited Sn as electrocatalyst.<sup>175, 176</sup> Figure 6 show a photo of the solar powered trailer that holds the CO<sub>2</sub> reduction reactor. Mantra Energy alternatives, a subsidiary of Mantra Venture Group, claims to be in the process of building a pilot plant capable of processing 100 kg of CO<sub>2</sub>.<sup>177</sup> Their reactor is based on prototypes and a patent by Oloman and Li.<sup>173, 174, 178</sup>

#### 4. ENERGY BALANCE ON THE REUSE OF CO<sub>2</sub>

As mentioned in the introduction, the reduction of CO<sub>2</sub> could be a way to store energy by using one of its products as an energy carrier. Methanol has been pointed out as the best choice among the CO<sub>2</sub> products in what is known as the Methanol Economy<sup>®</sup>.<sup>5, 179</sup> However, as mentioned in Section 2, the 6 electron reduction is not kinetically favorable and reports on the reduction to methanol have shown low current densities, typically in the order of 5 to 10 mA cm<sup>-2</sup>, with low to mid faradaic yields, i.e., below 40%.<sup>114, 180</sup> On the other hand, formic acid is a reduction product obtained with high faradaic efficiencies (> 70%) and moderate current densities<sup>130, 162, 164, 165</sup> however, direct formic acid fuel cell has not shown the same performance as DMFC.<sup>137</sup> Nevertheless, it is an interesting exercise to calculate the energy balance involved in the reduction of CO<sub>2</sub> to one of its products and subsequent use to generate electricity.

To obtain 1 kg of methanol from CO<sub>2</sub> would require a charge of 18.1 × 10<sup>6</sup> C and about 1.4 kg of CO<sub>2</sub>. Considering that the best faradaic efficiencies reported are ca 50%<sup>180</sup> the charge needed to obtain 1 kg of methanol would be then 36.2 × 10<sup>6</sup> C or 10 × 10<sup>3</sup> Ah. The potential needed to reduced CO<sub>2</sub> to methanol is below -0.5 to -0.6 V versus NHE<sup>180</sup> therefore, the power needed to obtain 1 kg of methanol is above 6 kW h. The theoretical value of the energy density for the oxidation of methanol to CO<sub>2</sub> is 6.1 kW h per kg of methanol.<sup>181</sup> The energy density generated by 1 kg of methanol in a DMFC would be 2.4 kW h corresponding to an overall efficiency of 40%, considering a complete oxidation to CO<sub>2</sub> and state-of-the-art technology. This represents 41% of the energy needed to obtain the initial kg of methanol by CO<sub>2</sub> reduction.

In the case that the energy carrier chose is formic acid, to obtain 1 kg would require 4.2 × 10<sup>6</sup> C and close to 1 kg of CO<sub>2</sub>. The faradaic efficiency for the CO<sub>2</sub> reduction to formic acid is in average ca. 80% at a potential of -1.6 V versus NHE<sup>162, 165</sup> demanding an energy of about 2.2 kW h. The theoretical value of the energy density for the oxidation of formic acid to CO<sub>2</sub> is 1.7 kW h per kg of formic acid. The energy density generated by



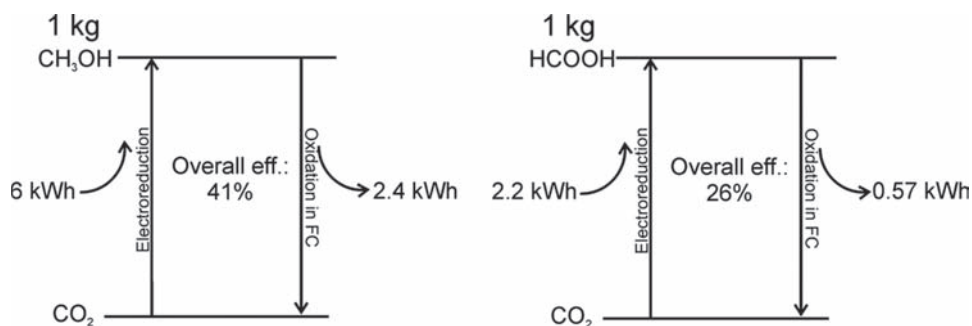


Fig. 7. Energy demand/output and overall efficiency for the electroreduction/oxidation process of CO<sub>2</sub> to/from methanol and formic acid.

1 kg of formic acid in a fuel cell would be 0.57 kW .h corresponding to an overall efficiency of 30%, considering a complete oxidation to CO<sub>2</sub> and state-of-the-art technology. The value represents 26% of the energy needed to produce 1 kg of formic acid by the reduction of CO<sub>2</sub>.

In both cases, the energy obtained from the oxidation of the mentioned fuels in a fuel cell is lower than the energy needed to produce those fuels. Figure 7 shows a schematic representation of the electroreduction/oxidation process for methanol and formic acid with the values of energy and overall efficiency. In this simple exercise, the energy needed to capture and deliver CO<sub>2</sub> to the electroreduction device has not been taken into account, so in the real process the difference should be even bigger for the total balance. Although, these results might seem discouraging, and the energy difference is expected as the thermodynamic dictates,<sup>182</sup> they show that there is still much to do in terms of finding better electrocatalyst for both the CO<sub>2</sub> electrochemical reduction and fuel cells, as well as improving the design of cells and devices to exploit the processes at a maximum and reduce the energy loss. On the other hand, there are few cases in the primary energy generation sector where electricity is generated without demand. For example in Germany the electricity generated by solar installation exceeds the need of the grid on given periods.<sup>183, 184</sup> Another example is in nuclear power plants, where it is desired that the power plant always works at a constant power output disregarding the variations demand in the grid. This mentioned excess could be currently used to electroreduce CO<sub>2</sub> even though the energy balance seems unfavorable.

## 5. CONCLUDING REMARKS

The reduction of CO<sub>2</sub> is foreseen as a way to replace fossil fuels while maintaining the CO<sub>2</sub> amount in the atmosphere. The electrochemical reduction of CO<sub>2</sub>, in particular, presents some advantages in comparison to the CO<sub>2</sub> chemical activation.

An overview of the vast literature on the subject shows that metal electrodes are most viable to scale up the process and that CO and formic acid are the most suitable

products in terms of faradaic efficiency and current density obtained. It was shown that the electrochemical reduction of CO proceeds with the simultaneous evolution of H<sub>2</sub>, which can produce directly syngas in the desired ratio for the FT process. From then, methanol and a number of C<sub>n</sub> ( $n > 2$ ) compound can be obtained. With regards of formic acid as an electroreduction product, has an economic value due to the industrial processes and products it is involved, can be used as a fuel in DFAFC, and also can be converted to methanol and from then to a number of C<sub>n</sub> compounds. Moreover, practical demonstrations of the reduction to formic acid at a pilot scale have been shown indicating that the process is viable and that the applicability will depend on the energy cost.

Nevertheless, scientific and technological challenges still remain. In terms of the electrocatalysts, those that show high specificity, like In or Sn for formic acid or Au for CO, present a high overpotential, demanding considerable energy for the reduction process and resulting in the formation of H<sub>2</sub> or other products. In terms of metals catalysts further study need to be conducted on bimetallic or trimetallic mixtures or alloys in order to decrease the reduction overpotential. Solubility of CO<sub>2</sub> is another issue, and although performing the reduction in aqueous media is interesting for simplicity, the low solubility compared to organic solvents is a disadvantage, forcing to work in pressurized systems in order to obtain current densities economically desirable ( $> 100 \text{ mA cm}^{-2}$ ). In this matter, gas diffusion type of electrodes have shown to be a way to work around the low CO<sub>2</sub> solubility issue. A key point to have in mind for future developments is the durability of electrodes and reactors, since high voltages and typically concentrated alkaline solutions are used. These are some of the issues to focus in order to improve the energy balance and therefore improve the economical aspect to make the CO<sub>2</sub> reduction a reality.

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