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Electrochemical reduction of carbon dioxide on flat metallic cathodes

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The most important methods for the electrochemical reduction of carbon dioxide on flat metallic cathodes have been systematically summarized using a novel classification approach. In contrast to the usual classification systems that were based solely on the products of electrolysis, the electroreduction procedures have been grouped according to both the nature of the cathode (sp or d group metal electrodes) and the solvent used for the supporting electrolyte (aqueous or nonaqueous solutions). The new classification system allows the identity of the electroreduction product to be better related to the nature of the metallic electrode and the supporting electrolyte. Similar reduction products are formed by each of the four possible combinations of electrodes and supporting electrolytes (sp group metals in aqueous and nonaqueous electrolytes, and d group metals in aqueous and nonaqueous electrolytes, respectively). The discussion has included both synthetic aspects and mechanistic considerations. Of special interest in this review is the discussion of procedures for the selective preparation of formic acid and for the manufacturing of hydrocarbons and/or alcohols using carbon dioxide as the carbon source.

1. Introduction

The large number of recent papers dealing with the electrochemical reduction of carbon dioxide are of both fundamental and preparative interest. The fundamental research is stimulated by the similarity of CO_2 electroreduction to photosynthesis, the latter being one of the most important reactions in nature and the basis of all living activity [1–3]. It has been the aim of chemists to utilize this naturally occurring process of carbon fixation as a model for manufacturing synthetic fuels [4]. Since 1870 there have been many attempts to find nonbiological approaches to the reduction of CO_2 to various organic compounds [2]. Different ways to reduce CO_2 have been researched, such as radiochemical, chemical, thermochemical, photochemical, electrochemical and biochemical procedures [3]. Since carbon dioxide is easily available in nature and huge amounts are generated by human activities, it is a practically infinite carbon source for the chemical industry, namely, for the manufacturing of alcohols (methanol and ethanol), aldehydes, hydrocarbons (methane and ethylene) and carboxylic acids (formic and oxalic acids). Among these products, methanol is an environmentally neutral liquid energy source. Thus electrochemistry is a viable means for removing CO_2 from the atmosphere, and converting it into more valuable chemicals [5]. Also, the synthesis of hydrocarbons by the electrochemical reduction of CO_2 might be of practical interest for fuel production and the storage of solar energy [6–8].

As seen in Fig. 1 the number of papers published on the electroreduction of CO_2 reached a maximum in 1986/1987, then slightly decreased until 1990, and continuously increased thereafter. In the last two years (1994/1995) the number of papers reached a constant level (57 and 58, respectively). The growth of the topic in the last decade is due to the promising results of electrochemical methods, which can be applied on the industrial scale. Many of these procedures are currently being patented. All these electroreduction techniques had to overcome the difficulty of finding electrodes with both a high electrocatalytic activity and a satisfactory lifetime. Also, given the relatively low solubility of CO_2 in aqueous solutions, methods for improving the solubility of CO_2 had to be found. A possible solution to this problem is to perform the electroreduction at high pressure or in nonaqueous solutions. Three kinds of electrodes are currently being employed: (i) bulk metal electrodes with appropriate electrocatalytic activity, (ii) chemically modified electrodes, and (iii) metal electrodes in the presence of electrocatalysts dissolved in the supporting electrolyte [9, 10]. Only electrodes belonging to the first category will be dis-

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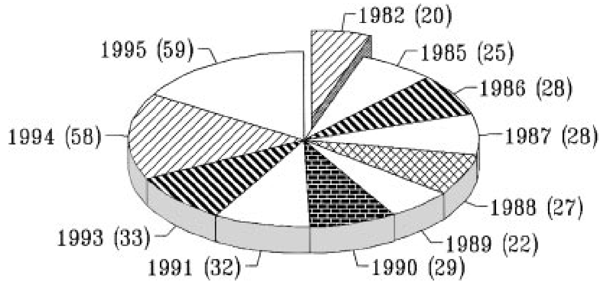


Fig. 1. Number of papers published in the last decade on the electrochemical reduction of CO_2 on flat metallic electrodes.

cussed here. Bulk metals can be considered suitable from the electrocatalytic standpoint if they have the ability to lower the overpotential while maintaining high current efficiencies and high current densities ($> 100\,\mathrm{mA\,cm^{-2}}$) [5].

Several classification systems have been used to systematize the impressive number of data accumulated in CO_2-related synthetic work [3, 11–14]. Most of these classifications are solely based on the nature of the main product obtained in the electrochemical synthesis. Four classes of metallic electrodes in aqueous supporting electrolytes and three classes for nonaqueous media can be distinguished [11–14]. Thus, in aqueous solution (i) metallic In, Sn, Hg and Pb are selective for the production of formic acid, (ii) metallic Zn, Au and Ag produce carbon monoxide, (iii) metallic Cu exhibits a high electrocatalytic activity for the formation of hydrocarbons, aldehydes and alcohols, while (iv) metallic Al, Ga and Group VIII elements (except Pd) show low electrocatalytic activity in CO_2 electroreduction [11–13]. In nonaqueous supporting electrolytes (i) on Pb, Tl and Hg the main product is oxalic acid [3]; (ii) on Cu, Ag, Au, In, Zn and Sn carbon monoxide and carbonate ions are obtained [3, 12, 14], while Ni, Pd and Pt are selective for CO formation; and (iii) Al, Ga and Group VIII elements (except Ni, Pd and Pt) form both CO and oxalic acid [12]. Additional classification criteria for the processes occurring in CO_2 electroreduction based on both the electrocatalytic properties of the electrode material and the nature of the supporting electrolyte would allow a better systematization of the multitude of reactions and would give more insight into the mechanisms controlling the phenomena.

In the early seventies, the difference between the electrocatalytic behaviour of electrodes made of sp group metals and of d group metals, respectively [15–27], was recognized as an important criterion in determining the selectivity of electrode processes. Thus, when used in aqueous supporting electrolytes, sp group metal cathodes, such as Hg, In, Sn and Pb favoured the electroreduction of CO_2 to formic acid [15–18, 24], while on d metals (e.g., on Pt and Pd) carbon monoxide was formed as the main product [26, 28]. Another typical d group metal, Ru, was found to exert favourable electrocatalytic properties for the preparation of various organic compounds: hydrocarbons (methane and ethylene), alcohols (methanol and ethanol) as well as formaldehyde [29–32].

However, the same groups of metals behaved differently in nonaqueous supporting electrolytes: on sp group metals (Tl, Pb and Hg) oxalic acid was selectively produced; on several d group metals (Fe, Cr, Mo, Ti and Nb) oxalic acid and CO were the main products; while on several sp group metal electrodes (In, Sn, Cd, Zn, Cu, Ag and Au) and d group metal electrodes (Pd, Pt and Ni) mainly CO was formed [10–12, 33–35].

This discussion of the electroreduction of CO_2 will consider both the importance of the cathode metal and that of the solvent. Therefore, the review comprises two main sections, according to the type of electrodes used as the cathode material (sp and d group metals). Given the influence of the solvent on the nature of the products in each Section separate subSections are dedicated to work in aqueous and in nonaqueous media, respectively. The new classification system allows the identity of the electroreduction product to be related to the nature of the metallic electrode and the supporting electrolyte. It is shown that similar reduction products are formed by each of the four possible combinations of electrodes and supporting electrolytes (sp group metals in aqueous and nonaqueous electrolytes, and d group metals in aqueous and nonaqueous electrolytes, respectively).

2. Electrochemical reduction of carbon dioxide on sp group metals

According to Kita [19] the sp metal group includes the principal group metals of the periodic table, and the transitional metals with completely filled d orbitals; that is, the metals with a d^{10} electronic configuration: Zn, Cd, Hg, Cu, Ag and Au.

2.1. *Electroreduction in aqueous solution*

Metals of the sp group have been used as the cathode material from the beginning of electrochemical research. Copper and zinc cathodes have probably been the most extensively employed in the electrochemical reduction of CO_2. In 1870, Royer [36] performed experiments on Zn electrodes using a sodium bicarbonate supporting electrolyte to obtain formic acid. At the beginning of the 20th century Coehn and Jahn [37] improved Royer's procedure by using Zn amalgam cathodes. The authors prepared formic acid with current efficiencies (r_f) up to 88.6%. Ehrenfeld [38] successfully raised the faradaic yield (r_f) of the process to 95% by using a divided cell equipped with Zn amalgam vs Pt electrodes, and an ammonium bicarbonate supporting electrolyte. Fischer and Prziza [39] were the first to use pressurized electrolysis cells in CO_2 electroreduction. They obtained formic acid with almost quantitative yields on Zn amalgam and Pb cathodes at pressures in the range from 5 to 50 atm. Both lead amalgam with 0.2 wt % Pb [40] and rotating amalgamated Cu cathodes [35] have proved efficient in the manufacturing of formic acid. To eliminate the polluting mercury involved in amalgam electrodes Kesarev and coworkers [16] reintroduced Royer's metallic Zn cathode, one hundred years after its first use. Watanabe and coworkers [41, 42] examined the electrocatalytic activity of Cu-based alloys. In their experiments electrodes of Cu–Sn and Cu–Zn alloys, as well as of elemental Cu, Sn and Zn, were used at low temperature (275 K). On these cathodes formic acid, methanol and carbon monoxide were produced. Noda and coworkers [10, 11] found that, in addition to Hg and Pb, metallic In and Sn were selective for producing formic acid, while metallic Al and Ga had scarcely any electrocatalytic activity for CO_2 electroreduction. In 1983, Kapusta and Hackerman demonstrated 90% current efficiency for formic acid generation during CO_2 reductions on In and Sn [43].

Ito and coworkers [17] reported the excellent electrocatalytic activity of several sp group metals for the synthesis of formic acid. Indium and cadmium, metals with a medium value of the overpotential for the hydrogen discharge reaction, were used as the cathode in a divided electrochemical cell. In aqueous carbonate solution at room temperature and current density (c.d.) from 5 to 10 mA cm^{-2}, faradaic yields from 70 to 80% were reached. It is notable that indium not only reduced CO_2 efficiently, but also inhibited hydrogen evolution. By using Sn as the cathode, the electrosynthesis of HCOOH could be achieved at higher c.d., that is, under kinetically favourable conditions. Unfortunately, the r_f of the process decreased, such that the advantage of the increasing productivity was negated by the poor selectivity. On other sp group metals: Zn, Pb and Cd, formic acid formed only at low or medium current efficiency. Work performed in 1985 by Bagotskii and coworkers [15] duplicated Ito's former results [17] related to the electrocatalytic activity of sp group metals.

In a more recent paper Ito and coworkers [18] discussed the product distribution as a function of the electrode material and the cathode potential (Table 1). It was found again that at moderate cathode potentials, indium electrodes are very suitable for HCOOH preparation (r_f = 87.6%, and selectivity S = 92.8%) [44]. The best yields for HCOOH were obtained on Hg (r_f up to 100%, at current densities of 10^{-7} to 10^{-2} A cm^{-2}), In and Pb, in an aqueous tetraethylammonium phosphate (TEAP) supporting electrolyte. When Sn and Zn cathodes were employed in aqueous TEAP solution the r_f ranged from 38 to 70%. Tin is a typical sp group metal (4th group), while Zn, a transitional element with d^{10} electronic configuration, is also considered an sp group metal [19–21]. Komatsu and coworkers [45] obtained HCOOH with up to quantitative r_f and good rates (10 mA cm^{-2}) on Bi and Bi-plated glassy carbon electrodes. In contrast, Sb was not effective in CO_2 electroreduction; with Sb-plated electrodes hydrogen was produced with only traces of HCOOH.

Table 1. Faradaic yields as a function of the electrode material and the cathode potential for the main products obtained in CO_2 electroreduction [*18*]

Cathode metal	*Potential vs SCE* /V	*HCOOH* /%	*CO* /%	*H_2* /%
In	–2.0	87.6	6.8	4.9
	–2.4	83.2	4.2	13.2
Pb	–2.0	72.9	2.0	15.6
	–2.4	78.9	2.1	14.3
Zn	–2.0	46.6	35.6	12.4
	–2.4	53.4	16.8	35.2
Sn	–2.0	67.5	9.1	29.9
	–2.4	37.6	4.2	61.6

The introduction of Cu and Cu-coated metallic electrodes for the preparation of hydrocarbons [28, 46–53] and alcohols [54, 55], or both hydrocarbons and alcohols [56–62] in aqueous media can be considered a real breakthrough [3]. These reductions were performed at ambient temperature and pressure at high current density. In addition to the simplicity of the method, when neutral supporting electrolytes were used, the r_f was of quantitative order [63–69]. One difficulty in using Cu electrodes is fast deactivation, usually observed 20–30 min after the beginning of the electrolysis [59]. A periodic anodic activation procedure allowed high hydrocarbon yields to be maintained over prolonged electrolysis runs. Similar conclusions were drawn by Cook and coworkers [63]; their work also revealed that the electrocatalytic activity of Cu depended on renewal of the electrode surface. On a clean Cu surface the achieved r_f values CH_4 and C_2H_4 were of 73% and 25%, respectively. The use of rotating disc electrodes ensured a constant transport to and from the Cu surface, since the product of the electrode reduction is continuously swept away from the surface of the disc [60]. The mechanism of CO_2 electroreduction on Cu is still not completely understood. No sufficient explanations were found for the behaviour of supported Cu electrodes, and for the influence of Cu^+ ions present in the supporting electrolyte [53, 60–62]. A recent study by Hwang and coworkers [53] aimed to evaluate the experimental factors affecting the r_f of methane and ethylene formation on Cu/glassy carbon cathodes. In their experiments performed in aqueous solution the highest r_f values (ca. 70%) were obtained at pH 7 (at room temperature) and at pH 2 (at ice temperature). Also, the surface area of the electrode (both its size and the number of Cu deposits on the glassy carbon) played an important role in the electroreduction of CO_2. The presence of Cu-complexing agents in the supporting electrolyte, such as ammonia, ethylenediamine or pyridine, enhanced the efficiency of the electrochemical reduction. Ikeda and coworkers [70] used copper-loaded gas diffusion electrodes for the mass reduction of carbon dioxide. Most of the products were similar to those obtained on a Cu plate electrode (e.g., CH_4, C_2H_4, C_2H_5OH, CO and $HCOO^-$) but the current densities achieved for porous electrodes were about two orders of magnitude greater. The highest r_f values for hydrocarbons and CO were achieved with electrodes manufactured of pure and small particle size Cu powder [70]. Recently, Komatsu and coworkers [71] introduced a copper-based composite electrode for the gas-phase electrochemical reduction of CO_2. These electrodes were made of copper deposited onto a solid polymer electrolyte. When Cu on a cation-exchange membrane (Nafion® 117) was used C_2H_4 was the main product, while Cu on an anion-exchange (Selemion AMV, styrene-divinylbenzene copolymer type) membrane was selective for HCOOH.

Although similar in their electronic configuration and alike in most of their chemical properties, Cu and Ag behaved differently, when employed as cathode in CO_2 electroreduction. By using an ab initio MP4 calculation Watanebe and coworkers [72] explained this difference. Their calculations suggested that CO did not interact with Ag, but that it was adsorbed on the Cu electrode, the C – O bond being weakened in the latter case. The optimized geometry and vibrational wavenumbers of $CuCO^-$ were determined, but there was no evidence for $AgCO^-$.

Improved r_f were achieved in the electroreduction of CO_2 at high pressure. Thus, in experiments performed with principal group cathodes at 30 atm, formic acid was obtained with excellent faradaic yields [73]: 95.5% on Pb, 92.3% on Sn, 90.1% on In, and 82.7% on Bi. Despite the similarity of In and Al, the latter metal had only low activity in CO_2 reduction and produced almost exclusively H_2 (86.5%) [73]. It should be noted here that in high pressure electrolysis glassy carbon and *n*-Si wafer cathodes reduced CO_2 efficiently to CO and HCOOH (carbon) and 46.3% HCOOH (*n*-Si) [73]. When glassy carbon electrodes were used, the pH of the supporting electrolyte was found to be significant with a slightly acidic oxalate solution being favourable for the efficient electroreduction of CO_2 [74]. It was necessary to activate the glassy carbon electrode by applying a 30 s anodic pulse at +1.2 V vs SCE [75]. Such an electrode showed enhanced activity, that is, the reduction occurred at lower cathodic potentials than on the glassy carbon electrode with no previous anodic conditioning.

Numerous reaction mechanisms were suggested [35, 44, 76, 77] for the electroreduction of CO_2 in aqueous media. Most of these mechanisms accept the steps shown in Fig. 2. Udupa [35] and Paik and Eyring [76, 77] assumed independently that the reactive species are the neutral hydrated CO_2 molecules that undergo the first electron transfer step to form $CO_2^- \cdot$ radicals (Fig. 2(a)). Such an initial step is likely for all sp group metal cathodes. However, analogous mechanisms were proposed for reactions proceeding on d metal electrodes. Estimates for the standard potential of the first electronation are about -1.87 ± 0.02 V vs SCE. However, in most experiments this potential is probably lower because the surface concentration of the radical is below the standard conditions, and the energy is associated with the adsorption of the radical onto the electrode surface [5, 78]. It was suggested that the $CO_2^- \cdot$ radical may be formed by photoemission [24, 69]. The adsorbed $CO_2^- \cdot$ radicals (Fig. 2(b), then react with the water molecules, also adsorbed at the electrode surface, to form $HCO_2 \cdot$ radicals (and OH^- ions). Due to its unpaired electron this intermediate remains adsorbed at the electrode surface until it undergoes the second reduction step to HCO_2^- (Fig. 2(c)). At this instant the anionic HCO_2^- species is rejected from the metal surface into the bulk phase (Fig. 2(d)). In several cases voltammetric plots provide valuable information about the reduction mechanism. Thus, when Hg electrodes were used the slope of the voltammetric plot at low c.d. was about 450 $\mu A\,cm^{-2}\,V^{-1}$, while at high c.d. the slope increased by almost one order of magnitude (3600 $\mu A\,cm^{-2}\,V^{-1}$). This significant difference can be attributed to different rate determining steps [44]. Similar shapes but different Tafel slopes of the polarization curves were recorded on other metals [16].

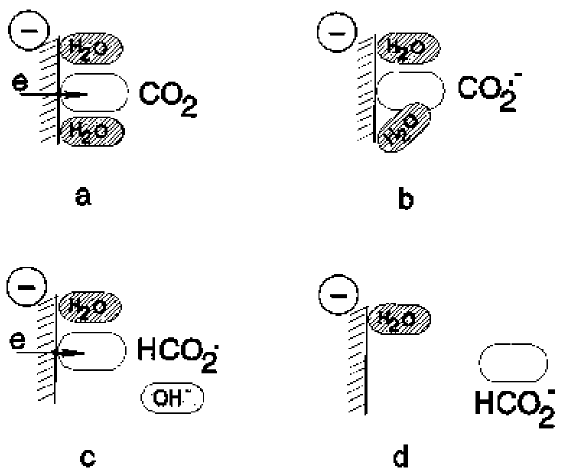


Fig. 2. Mechanism of CO_2 electroreduction on sp group metal electrodes [35, 44, 76–78]. Neutral hydrated CO_2 molecules **(a)** undergo electronation to yield in adsorbed $CO_2^- \cdot$ radicals; **(b)** the latter react with adsorbed water molecules to form adsorbed $HCO_2 \cdot$ radicals and OH^- ions; **(c)** $HCO_2 \cdot$ radicals remain adsorbed at the electrode surface and undergo further reduction to formate ions; **(d)** the negatively charged $HCOO^-$ ions are rejected from the electrode surface.

Several studies revealed that the current efficiency of CO_2 electroreduction depended on the nature of the cation and anion present in the supporting electrolyte. It was noted that the presence of CO_3^{2-} or SO_4^{2-} anions in the solution increased the r_f, while PO_4^{3-} did not enhance the faradaic yield [9, 18, 24–27]. The r_f improvement by CO_3^{2-} and HCO_3^- is probably due to the direct participation of these anions in the mechanism of CO_2 electroreduction. Therefore, the true mechanism of CO_2 electroreduction appears to be more complicated than that initially assumed. Spichiger-Ulmann and Augustynski [26, 27] attributed the high cathodic currents recorded in aqueous $CsHCO_3$ solution to the participation of HCO_3^- ions in the electroreduction of CO_2. The authors assumed that HCO_3^- ions were the species to undergo electroreduction rather than the neutral CO_2 molecules. For different anions present in the supporting electrolyte the r_f of HCOOH formation increased from 35 to 87.5% in the order: $PO_4^{3-} < SO_4^{2-} < CO_3^{2-} < HCO_3^-$. These data can be explained by considering the electrosorption of the hydrated ions at the electrode surface. This phenomenon is also known for other electroreduction processes [13, 21, 79–84]. Small cations, such as Li^+ and Na^+ are not adsorbed at the electrode surface, due to their strong hydration. In addition, small cations carry to the cathode a large number of water molecules, and thus supply protons for the electroreduction [80]. Conversely, the less hydrated bulky cations are preferentially adsorbed at the cathode. Depending on the nature of the cation present in the supporting electrolyte the current efficiency of the process increased from 47 to 90% in the order: $Rb^+ < K^+ < Na^+ < Li^+$. In a recent paper, Kyriacou and Anagnostopoulos [85] reported r_f of ethylene increasing with the cation in the order $Cs^+ \approx K^+ > Li^+$. The nonmetallic cation NH_4^+ allowed only hydrogen evolution with almost quantitative r_f ($\approx$ 92%). Apparently, the described behaviour is related to the radius of the cation. However, we believe that the hydration of the metal ions plays a key role in controlling the selectivity of CO_2 electroreduction.

Potentiostatic CO_2 reduction studies performed by Ito [17, 18, 86] and Komatsu [45] in neutral $KHCO_3$ solution showed that: (i) Hg, In, Sn, Pb and Bi favoured the formation of HCOOH and $HCOO^-$; (ii) Zn and Cd, both with d^{10} electronic configuration (i.e., sp group metals) exhibited poor electrocatalytic properties in the synthesis of HCOOH (e.g., on Zn 20% $HCOO^-$ and 40% H_2 were obtained, while on Cd 39% $HCOO^-$ and 39% H_2 were observed; (iii) the main product on Ag and Au was carbon monoxide; (iv) all other metals produced hydrogen only; and (v) the favourable properties of indium suggested the opportunity of testing the electrocatalytic activity of other 3rd group metals.

Diverse new electroreduction products were obtained by Eggins and co-workers [87] in an aqueous quaternary ammonium salt (QAS) solution. Thus, on Hg and graphite, oxalate anions formed, on Pb, glyoxylic acid was observed, while on Hg malic acid was obtained. Similar results were reported by Bewick [88, 89], Wolf and Rollin [90] and Kuhn [91]. The presence of glyoxylic acid among the reaction products was in agreement with the previously known reduction of oxalate to glyoxalate (on Pb cathodes) [92]. The reaction mechanism of glyoxalate formation was investigated by cyclic voltammetry in aqueous tetramethylammonium chloride solution. Two reduction steps were evidenced at −0.68 and −1.4 V vs SCE. The authors suggested the following mechanism:

$$CO_2 + e^- \longrightarrow CO_2^- \cdot \qquad (1)$$

$$CO_2^- \cdot + CO_2^- \cdot \longrightarrow \underset{\text{(oxalate)}}{^-O_2C - CO_2^-} \qquad (2)$$

$$^-O_2C - CO_2^- + 3H^+ + 2e^- \longrightarrow {}^-O_2C - CH(OH)_2 \longrightarrow \underset{\text{(glyoxalate)}}{^-O_2C - CHO + H_2O} \qquad (3)$$

As seen, the mechanism of oxalate formation involves the monoelectronic reduction of CO_2 (Equation 1), followed by the dimerization of the $CO_2^- \cdot$ radical (Equation 2). The latter step is favoured by the presence of a QAS in the aqueous supporting electrolyte. The reduction may stop here or the dinegative oxalate ion may eventually undergo further reduction to glyoxalate (Equation 3).

The preparative electrosynthesis carried out on a graphite electrode at −0.9 V vs SCE yielded in oxalate ions (r_f = 78%), but the nature of the products varied as a function of the cathode potential (Table 2) [87–91]. However, in other electroreduction experiments performed on graphite at the same cathode potential (−0.94 V vs SCE), methanol was obtained with excellent faradaic yield (r_f = 100%), provided that the current density was maintained at low values (33–100 μA cm^{-2}) [5]. Good oxalate yields were also obtained with Pb cathodes at relatively moderate cathode potentials (see entry at −1.26 V vs SCE in Table 2) [92].

Many studies were concerned with the electroreduction of CO_2 on Au and Ag electrodes. Ito [16, 17] obtained CO, H_2 and $HCOO^-$ on gold. The nature of the product was determined by the cathodic polarization; for example, from −1.3 to −1.6 V vs SCE exclusively CO and H_2 were formed. In galvanostatic experiments Hori and coworkers [46–48] obtained $HCOO^-$, CO, CH_3OH, CH_4 and C_2H_4. When the Ag electrode was polarized to −0.8 V vs SCE methanol was obtained with good current yields ($r_f \leq$ 78%), but at very low current densities (11 μA cm^{-2}) [78]. At cathode potentials more negative than −1.4 V vs SCE exclusively carbon monoxide formed [78]. The presence of CO, ethane and methane among the reaction products was also evidenced by Noda [32]. The cathode potential was again found to determine the magnitude of the products yields. A variety of possible pathways account for this. It was concluded that the most appropriate cathodic potentials (with respect to Ag/AgCl) for the preparation of different products were as follows:

$HCOO^-$	CO	C_2H_4	CH_4
$E = -1.4\,V$	$E = -1.52\,V$	$E = -1.58\,V$	$E = -1.70\,V$

Furthermore, new reaction products such as alcohols and aldehydes, were detected. At −1.65 V vs Ag/AgCl, 14% ethanol was formed. Kostecki and Augustynski

Table 2. Faradaic efficiency (%) of the formation of three representative CO_2 electroreduction products on graphite [91] and Pb [92] electrodes (in aqueous 0.1 mol dm^{-3} NH_4Cl supporting electrolyte, at room temperature)

Electrode	*E_c vs SCE / V*	*Oxalate*	*Formate*	*Glyoxylate*
Graphite	–0.900	100	–	–
	–1.05	10	78	12
	–1.26	17	74	7
	–1.70	15	72	–
	–1.88	6	65	28
Pb	–1.26	44	55	–
	–1.40	9	90	–
	–1.49	25	74	–
	–1.65	1	62	35

[93] investigated the poisoning of a polycrystalline Ag cathode during the electroreduction of CO_2 to CO. Surface species closely similar to the detected poison were obtained by immersing the Ag electrode at open-circuit in a dilute formaldehyde solution. As for the copper cathodes, a periodic anodic stripping of the Ag surface was efficient in removing the inhibiting species, and producing stable current densities and r_f of CO formation over 4–5 h electrolysis runs.

The critical overview of the published results on CO_2 electroreduction lead to the conclusion that: (i) on sp metal electrodes in aqueous supporting electrolytes the main product was typically formic acid; and (ii) the electrocatalytic activity of the cathode decreased in the following order: In ≈ Bi > Hg > Pb > Sn > Zn ≈ Cu > Cd > Ag > Au ≫ Sb.

2.2. *Electroreduction in nonaqueous media*

The original reasons for using nonaqueous supporting electrolytes were to increase CO_2 solubility and to suppress hydrogen evolution and, thereby, to increase the current efficiency [5]. However, these investigations also demonstrated that dimerization processes occurred with the formation of higher valued C_2 products, rather than the electroreduction to methanol or methane [5].

In most organic solvents CO_2 has not only a much better solubility than in water, but this solubility is unrelated to the dielectric constant of the solvent [3]. For example, the solubility of CO_2 in dimethyl sulfoxide (DMSO) and acetonitrile (AN) is about four times that in water, while its solubility in propylene carbonate (PrC) is about eight times greater. Dimethylformamide (DMF) has proved the best solvent of CO_2, with a 20 times greater solubility than in water [94]. However, recently Chang and coworkers [95] found that at elevated pressure CO_2 showed a solubility order in which cyclohexanone had the highest solubility of CO_2, toluene an intermediate solubility, and DMF the lowest solubility of CO_2 in the studied solvents.

Carbon dioxide electroreductions performed on Pb, Tl and Hg electrodes in nonaqueous media yielded oxalate ions [3], according to the mechanism shown in Equations 1 and 2. On other sp group metals (e.g., In, Zn, Sn and Au), a reductive disproportionation of CO_2 occurred, with the formation of CO and carbonate ions (Equation 4):

$$CO_2^{-}\cdot + CO_2 \xrightarrow{e^-} CO + CO_3^{2-} \qquad (4)$$

This process was first recognized by Saveant and coworkers [96, 97] in their studies of the uncatalysed electroreduction of CO_2. (The radical $CO_2^{-}\cdot$ was generated in the one electron reduction of the substrate molecule, according to Equation 1).

In chronopotentiometric reductions on Au and Hg electrodes in anhydrous DMSO [98], CO molecules were detected. Similar reduction mechanisms were assumed for both metals, with the rate determining step being the electron transfer to CO_2 (Equation 1). However, the standard reduction rate constants were significantly lower for Hg (3.2×10^{-25} cm s^{-1}) than for Au (4×10^{-12} cm s^{-1}). No evidence for the participation of the solvent in the redox process (Equation 2) was found, and no reasonable explanation for the very low rate constant at Hg electrodes was provided.

Vassiliev and coworkers [99] investigated the electroreduction of CO_2 on Sn, In, Pb and Hg in various nonaqueous solvents (DMF, DMSO, AN). In all of these experiments the main reaction was the dimerization to oxalate ions. The reaction mechanism suggested by the authors involved three steps (Equations 5–7):

$$(CO_2)_{ad} + e^- \longrightarrow (CO_2^{-}\cdot)_{ad} \qquad (5)$$

$$(CO_2^{-}\cdot)_{ad} + (CO_2)_{ad} \longrightarrow (O_2C - CO_2^{-}\cdot)_{ad} \qquad (6)$$

$$(O_2C - CO_2^{-}\cdot)_{ad} + e^- \longrightarrow {}^{-}O_2C - CO_2^{-} \qquad (7)$$

Unlike the mechanism in aqueous solutions which involves the dimerization of two radical anions (Equation 2), it can be assumed that the adsorbed radical anion attacks an adsorbed CO_2 molecule in nonaqueous media (Equation 6). This step is considered fast at all potentials.

Electroreductions of CO_2 were performed by Ito and coworkers [33] in an electrolyte consisting of a quaternary ammonium salt (tetraethylammonium perchlorate, TEAP) in DMSO or propylene carbonate (PrC). On Pb electrodes oxalic acid was the principal product ($r_f \leq 80\%$), while on Sn and In cathodes carbon monoxide was primarily produced. When zinc electrodes were operated under similar conditions, a mixture of oxalic acid, glyoxylic acid and CO was obtained, with an overall r_f of ~ 40%. The same authors [12] extended their investigation (in TEAP/PrC supporting electrolyte) to Pb, Tl and Hg electrodes that have proved suitable for the selective production of oxalic acid ($r_f \leq 84\%$). Oxalic acid was synthesized, under the form of its Zn salt, on a preparative scale. The procedure required the use of an undivided cell, equipped with a bulk Pb cathode in conjunction with a soluble Zn anode (the supporting electrolyte was tetrabutylammonium perchlorate in DMF). Good material yield (ca. 85%) and r_f (80%) were achieved for HCOOH [34]. When the reduction was accomplished at −2.8 V vs SCE (on a Pb cathode in TEAP/PrC), the concentration of oxalic acid increased almost linearly with temperature, up to 423 K [12]. Above this temperature limit, glyoxylic acid and glycolic acid started to form [12]. These observations are in agreement with a previously suggested mechanisms in which glyoxylic and glycolic acid were obtained by the further reduction of oxalic acid (see Equation 1) [58]. Glyoxylic acid was also obtained on Cd [12]. However, in this case the main reduction product was CO. In addition to oxalic acid and the already mentioned glycolic and formic acids, several other carboxylic acids were obtained during CO_2 electroreduction on sp group metals in nonaqueous solution [5, 100]. Examples include tartaric acid (on

Pb and Zn), malonic acid (on In, Zn, Sn and Pb), propionic acid (Zn, Sn and Pb), and *n*-butyric acid (on In, Sn and Pb). The best non-aqueous reductions occur on Pb and Sn, with maximum current efficiencies on the order of 50% on a lead cathode. However, current densities are generally low (≤ 10 $mA\,cm^{-2}$) [101].

Recently, CO_2 electroreduction experiments were performed on a Cu cathode in a benzalkonium chloride/methanol supporting electrolyte [49, 50] at low temperatures. At 258 K the composition of the products was CO (24.0%), CH_4 (39.1%) and C_2H_4 (4.4%) [49]. This means that the r_f of both CH_4 and C_2H_4 was better in pure methanol than in aqueous catholytes. Another advantage of the latter procedure consisted in the improved solubility of CO_2 in methanol (about five times that in water at ambient temperature). In 1995, Mizuno and coworkers [102] improved this method by cooling the same supporting electrolyte to an even lower temperature (243 K). Under optimal conditions, the r_f of CH_4 exceeded 42%. In addition, the efficiency of the competing hydrogen evolution was diminished to less than 8% at low temperatures. Methanol is a solvent which allows the electroreduction of highly concentrated CO_2 solutions [103]. The mole fraction of CO_2 is 0.34 at 4.0 MPa, and 0.94 at 5.8 MPa [104]. In such highly concentrated solutions the supply of CO_2 to the electrode is sufficient for the reduction to proceed with high current density. The main products of this electroreduction in the presence of tetrabutylammonium (a hydrophobic environment) were CO($r_F \leq 48.1\%$), CH_4($r_F \leq 40.7\%$), C_2H_4($r_F \leq 9\%$) and $HCOOCH_3$ ($r_F \leq 34.6\%$). In contrast, Li salt supporting electrolytes (a hydrophilic environment) enhanced the formation of methyl formate [103]. The formation of the methyl formate was explained by two consecutive processes: (i) the two-electron reduction of CO_2 to HCOOH, according to the usual mechanism in protic media (Equations 5 and 8), methanol serving as the protic solvent in this system, and (ii) the subsequent chemical esterification of formic acid with methanol (Equation 9):

$$CO_2^- \cdot + 2H^+ + e^- \longrightarrow HCOOH \qquad (8)$$

$$HCOOH + CH_3OH \rightleftharpoons HCOOCH_3 + H_2O \qquad (9)$$

When the high current density electroreduction on a Cu cathode was conducted at elevated pressure [103], the formation of CO was no longer limited by the mass transfer of CO_2. At 40 atm and –2.3 V vs Ag quasi-reference electrode the total current density was 436 $mA\,cm^{-2}$, while the r_f of CO_2 reduction reached 87%. In the gas phase CO, CH_4, C_2H_4 and H_2 were detected as products, while the main components present in the liquid phase were methyl formate and dimethoxymethane ($CH_3O - CH_2 - OCH_3$) [103]. Methanol is currently being used in industry as a CO_2 absorber. Therefore, the systems above may have industrial applications in large-scale methane production.

In summary, with sp group metal cathodes in aqueous supporting electrolytes the main product was formic acid (in neutral solution) and formate ions (in alkaline solution), while in nonaqueous media oxalate ions were preponderant [101].

3. Electrochemical reduction of carbon dioxide on d group metals

3.1. *Experiments in aqueous solution*

3.1.1. Ni, Pd and Pt electrodes. Platinic metals generally exhibit favourable electrocatalytic properties for the electroreduction of CO_2 due to the strong adsorption of CO_2 on these metals. It was shown that the active species on platinic metals were similar to the intermediates of methane oxidation [29–31]. However, the nature of products obtained on Pt, Pd and Ni was controlled by the experimental conditions [105–135]. Cyclic voltammetry performed at Pt cathodes evidenced three intermediates generated from the adsorbed CO_2 [6]. Maier and coworkers [113] investigated the influence exerted by the temperature and prepolarization upon the adsorption of CO_2 at Pt electrodes. At high temperatures, following a short anodic prepolarization (at + 0.520 V vs SCE), adsorbed (COOH) species were evidenced. Subsequent to prepolarizations effectuated at a more positive electrode potential (+0.650 V vs SCE, for 30 min), the adsorbed species were mainly $(CO)_{ads}$. The oxidation peak at +0.280 V vs SCE found in cyclic voltammograms was assigned to the adsorption product $(HCOOH)_{ads}$.

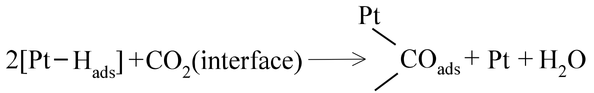
An impressive number of fundamental studies have been completed for the electrochemical reduction of CO_2 on the three basal planes of platinum: Pt(1 0 0), Pt(1 1 0) and Pt(1 1 1) [116–120, 136, 137]. In acidic solution the most active was the Pt(1 1 0) surface, which generated CO, while Pt(1 1 1) surface was inactive. The amount of reduced CO_2 increased when defects were present at the surface; these defects blocked preferentially the (1 0 0) terraces, whereas edge sites were less active for the adsorption. The formation and accumulation of CO at the Pt(1 1 0) surface was the result of the reduction of either HCO_3^- ions or of neutral CO_2 molecules produced by the dissociation of hydrogen carbonate ($HCO_3^- \rightleftharpoons CO_2 + OH^-$) [118, 119, 137]. The amount of CO_2 accumulated at different Pt single crystals is proportional to the maximum charge amount of oxidation of reduced CO_2: ~ 300 $\mu C\,cm^{-2}$ at Pt(1 1 0), and ~ 90 $\mu C\,cm^{-2}$ at Pt(1 0 0), respectively [137]. Even well-ordered Pt(1 1 1) single crystal electrodes became active for CO_2 adsorption by activation in the Pt oxide potential region [120]. This treatment induced disorder at the surface, and the electrocatalytic activity of the electrode increased. No differences in the nature of reduced CO_2 were observed at various adsorption potentials. Therefore, it is believed that carbon dioxide reacts with the adsorbed hydrogen to produce reduced CO_2 at the Pt surface. The mechanism of this process is not clear yet, and the structure of the reduced CO_2 is controversial [137]. Species proposed for the reduced CO_2 on polycrystalline Pt include: linear – CO_{ads} [138], bridged > CO_{ads} [139], —COOH [140–144] and ≡COH [144, 145]. Fourier transform i.r. spectra showed that both linear–CO (with a monopolar absorption band at 2030–2020 cm^{-1}) and traces of bridge-bonded CO (a bipolar band between 1850 and 1750 cm^{-1}) were formed on a polycrystalline Pt surface [118, 119, 136].

Taguchi and Aramata [137] suggested a three step mechanism for the formation of adsorbed linear CO (Equations 10, 11 and 12a), and adsorbed bent CO (Equations 10, 11 and 12b), respectively:

$$H^+ + e^- + Pt \longrightarrow Pt\text{–}H_{ads} \quad (10)$$

$$CO_2(\text{solution}) \longrightarrow CO_2(\text{interface}) \quad (11)$$

$$2[Pt - H_{ads}] + CO_2(\text{interface}) \longrightarrow Pt - CO_{ads} + Pt + H_2O \quad (12a)$$



$$2[Pt - H_{ads}] + CO_2(\text{interface}) \longrightarrow \begin{matrix} Pt \\ \diagdown \\ \end{matrix} CO_{ads} + Pt + H_2O \quad \text{(Pt)}_2CO_{ads} \quad (12b)$$

In this mechanism Equation 12(a) and (b) do not necessarily represent elementary steps.

While in contact with CO_2-saturated aqueous solution, the Pt surface became covered with a strongly attached 'reduced CO_2' layer [32]. This adsorption layer hindered the further electroreduction of CO_2, so that it could have never been quantitatively reduced. Thus the main process on Pt electrodes was hydrogen evolution. However, recent work by Inuzuka [112] described a cell based on a proton-conductive solid electrolyte with a porous Pt anode on one side, and a porous catalytic metal cathode on the other side. This patented apparatus was effective in the electrochemical reduction of CO_2 to methane and methanol.

In experiments performed using bulk Pd cathodes [24, 25] HCO_3^- was the electrochemically active species. The electrocatalytic properties of Pd paralleled its already proven superior catalytic properties in the chemical reduction of CO_2 [105]. This allowed the electroreduction of carbon dioxide to $HCOO^-$ with high current efficiencies [106–109].

Using the insertion of hydrogen, Ayers and Farley [110] proposed a new reduction method of CO_2/HCO_3^- on flat bipolar Pd electrodes. In this procedure, the atomic hydrogen penetrated the negative side of the bipolar Pd electrode. Once arrived at the opposite, positively polarized side of the electrode, hydrogen reduced the neutral CO_2 molecule, according to the mechanism shown in Equations 13–15:

$$(HCO_3^-/CO_2)_{ads} + 2Pd - H \longrightarrow HCOOH + 2Pd \quad (13)$$

$$(HCO_3^-/CO_2)_{ads} + 4Pd - H \longrightarrow HCHO + H_2O + 4Pd \quad (14)$$

$$(HCO_3^-/CO_2)_{ads} + 6Pd - H \longrightarrow CH_3OH + H_2O + 6Pd \quad (15)$$

Carbon dioxide molecules were adsorbed to the slightly positive face of Pd. No oxidation of the intermediates occurred.

It might be of synthetic interest that CO_2 electroreduction must not necessarily stop at alcohols. Experimental conditions can be found that drive the reduction to hydrocarbons. Thus, Azuma [111] researched the possibility of obtaining C_1–C_6 hydrocarbons. In their experiments of bulk Pd electrodes only low current efficiencies were achieved. Ohkawa and coworkers [56, 57] observed an increase of the r_f of both CO and HCOOH following the adsorption of the hydrogen onto the Pd electrode. It was postulated that the electrochemical hydrogen evolution was suppressed upon loading the electrode with molecular hydrogen from an external source. Adsorbed hydrogen may also react with the intermediates. The Tafel plots for CO_2 electroreduction on H-loaded Pd were compared to those recorded on H-free Pd electrodes [57]. The competing desorption of hydrogen was found to enhance the electrochemical reduction of CO_2. Hashimoto and coworkers [58] used the hydrogen accumulated in a Pd working electrode for the reduction of CO_2. In aqueous $KHCO_3$ solution HCOOH and CO were obtained. When the electrode was formed from Cu and Pd, methane and methanol were obtained in addition to HCOOH. The same authors [58] have also employed electrodes formed of a combination of sp and d group metals: Cu and Pd. For Cu electrodes modified with Pd the current efficiencies for the three products were larger than for Pd electrodes modified with Cu. The enhancement of the process efficiency was caused by the amount of hydrogen adsorbed by the working electrode, rather than by the change in the lattice morphology or the oxidation state of copper.

Both Pt and Pd electrodes were efficient in the preparation of methanol [121, 122]. Experiments were performed in slightly acidic supporting electrolytes (pH 5.0) to which a homogeneous catalyst was added under the form of pyridinium ions. In this method, the substrate reduction benefitted from the hydrogen released from two sources: the electroreduction of H^+ and from the pyridinium ions. The faradaic yields reached 30%. The main advantage of this procedure was that the electrochemical reduction of CO_2 proceeded at low overpotentials. New equipment has recently been patented for the electrochemical reduction of CO_2 on platinic metals [123–125]. The electrolysis cell used by Inuzuka [123] was equipped with a sandwich-type three-layer electrode, formed of a porous platinum-group metal anode, a proton-conductive solid electrolyte, a porous electrocatalytic metal cathode, and a second anode, facing the side of the cathode opposite to the first anode. The electrolytic solution contained the dissolved CO_2, and an ultrasonic vibrator completed the system. Due to the construction of the cell and to the electrocatalytic activity of the cathode layer, this set-up allowed for the efficient reduction of CO_2 over a long time period. The other cell, suitable for the synthesis of HCOOH, had a gas-diffusion electrode (formed of a reactive layer supported with Pd or its alloy), opposed by another gas-diffusion electrode, with a reactive layer supported with a Pt catalyst [124]. An ion-exchange diaphragm was positioned between the electrodes. Carbon dioxide was supplied from the back side of the first electrode, while hydrogen was fed from the reverse side of the other electrode. Aqueous carbonate and hydroxide solutions were introduced into the spaces between the electrodes. This setup allowed both for the efficient formation of the CO/HCOOH mixture and the generation of electricity. In an improved version of this apparatus, an electrocatalytic layer of platinic metal was deposited at the electrode surface to convert the O_2 in the CO_2 gas into water. As a result, high r_f for HCOOH was obtained in a nitrite-containing supporting electrolyte [125]. At present, preparative syntheses of formic acid are commonly being carried out on Pd electrodes at potentials higher than the reversible hydrogen potential, with current efficiencies close to 100% [126, 127]. For reductions performed in alkaline aqueous supporting electrolytes (pH8–10) at ambient pressure, the current yield for $HCOO^-$ was close to 100%. It is believed that adsorbed hydrogen atoms took part in the slow step of the HCO_3^- electroreduction.

Nickel has been used intensively for CO_2 electroreduction [54]. According to Hori and coworkers [47], mostly hydrogen gas evolved on Ni when the electrolytes were neutral or mildly acidic solutions. In addition to hydrogen Frese [101] obtained some carbon monoxide ($r_f = 9\%$). In recent studies Koga and coworkers [128, 129] found that 99.99% pure Ni electrodes in aqueous supporting electrolytes were suitable for producing hydrocarbons (methane, ethylene, ethane) and ethanol, as well. However, the simultaneous formation of hydrogen could not be avoided [128]. The reactive intermediate was CO, strongly adsorbed at the Ni surface. This adsorbed CO layer occupied most of the surface sites where hydrogen evolution usually evolved, and thus inhibited the hydrogen gas formation. The presence of adsorbed CO was evidenced by Fourier transform i.r. spectroscopy [129]. The same authors obtained hydrocarbons and traces of ethanol on pure Ni electrode (in a neutral phosphate buffer solution under an inert atmosphere of Ar and CO_2) [129]. Faradaic yields were: CH_4 (3.7%), C_2H_4 (0.1%), C_2H_6 (0.7%), and ethanol (0.1%), respectively. Voltammetric studies revealed that H_2O reduction started at –0.45 V vs SHE under Ar atmosphere (a potential at which CO_2 was also reduced to CO), while the anodic oxidation of the Ni was observed at –0.18 V vs SCE. Koga and co-workers [130] found CO molecules adsorbed at the Ni electrode, as the intermediate of CH_4, C_2H_4, and C_2H_6.

A novel trend is to use nickel cathodes at high pressure [131, 132]. As already mentioned, the low solubility of CO_2 in aqueous solutions is one of the major problems in designing a useful technology for the electroreduction of carbon dioxide. The concentration of CO_2 in water at 298 K is only 0.033 mol dm^{-3}. This can be increased at room temperature to 1.17 mol dm^{-3} at an elevated pressure (60 atm, a value close to the liquefying pressure of approximately 70 atm). Comparative mechanisms of high pressure CO_2 electroreduction (A) and the electroreduction of CO_2 at atmospheric pressure (B) are shown in Fig. 3 [131]. In the first case (Fig. 3A) the hydrogen atoms formed at the electrode surface by the reduction of water are consumed in the reaction with adsorbed CO_2 to form reduction products (mainly CO and HCOOH). In contrast, at a pressure of 1 atm most of the adsorbed hydrogen is desorbed under the form of H_2 (Fig. 3B). The ratio of adsorbed $CO_2^-\cdot$ radicals vs adsorbed hydrogen atoms increases with increasing pressure [131]. Ito and coworkers [133, 134] reported that several Group VIII metal electrodes, such as Fe, Co, Ni, Pd and Pt, ensured current efficiencies up to 62% in the electrochemical CO_2 reduction at high pressures (50–60 atm).

In 1993, Kudo and coworkers [131] studied the high-pressure CO_2 electroreduction on high purity Ni cathodes (in aqueous $KHCO_3$ supporting electrolyte, using 99.9% CO_2). It was found that the increase of CO_2 pressures favoured the r_f of CO_2 reduction and diminished the hydrogen evolution by water reduction. Best hydrocarbon yields were achieved at –1.6 V vs Ag/AgCl at 303 K. A more negative cathodic polarization enhanced the r_f for both CO and HCOOH. Also, the weight distribution of the hydrocarbons agreed with the Schultz–Flory distribution, suggesting a formation mechanism similar to thermally catalysed Fischer–Tropsch reaction. A possible scenario of the hydrocarbon formation at the Ni surface may involve the following steps: the electrochemical reduction of CO_2 to CO (Equation 16), simultaneous to and competing with water reduction (Equation 17). Next, CO is chemically reduced to adsorbed $=CH_2$ groups

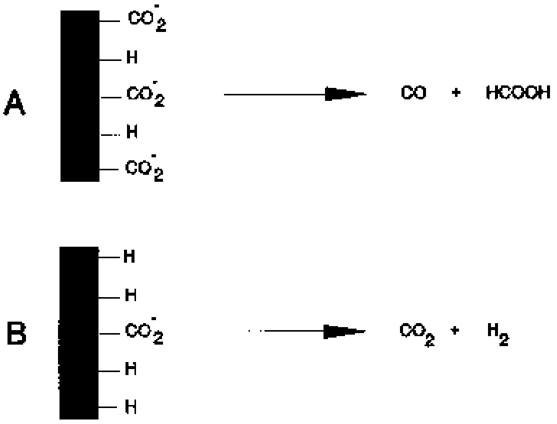


Fig. 3. Comparative mechanisms of high pressure CO_2 electroreduction (A) and the electroreduction of CO_2 at atmospheric pressure (B) on Ni cathode [131].

(Equation 18), and hydrocarbons form by surface polymerization of carbene groups (Equation 19):

$$CO_2 \xrightarrow{+e^-} CO_{ads} \quad (16)$$

$$H_2O \xrightarrow{+e^-} H_{ads} \quad (17)$$

$$CO_{ads} + 4H_{ads} \longrightarrow (=CH_2)_{ads} + H_2O \quad (18)$$

$$(CH_2)_{ads} \longrightarrow \text{hydrocarbons} \quad (19)$$

At cathode potentials below −1.9 V vs Ag/AgCl, mainly CO and HCOOH were produced. At such negative potentials the hydrocarbon formation process, which needs hydrogen, becomes disadvantageous. In this case, when CO_2 is reduced efficiently, both the electrons and hydrogen atoms were mainly consumed in the first reduction step, yielding CO and HCOOH. Carbon monoxide was obtained by its desorption from the Ni surface (Equation 20), forced by the high pressure of CO_2. Formic acid was generated by a different electrochemical pathway (Equation 21):

$$CO_{ads} \longrightarrow CO \uparrow \quad (20)$$

$$CO_2 + 2H_{ads} \longrightarrow HCOOH \quad (21)$$

A novel *in situ* i.r. spectroscopic technique, SNIFTIRS (substractively normalized interfacial Fourier transform i.r. spectroscopy) was used by Hori and coworkers [135] to provide convincing evidence of adsorbed CO at the Ni cathodes. In a CO-saturated phosphate buffer solution (pH 6.8) adsorbed carbon monoxide was present at the Ni electrode surface in the potential range from –0.4 to −0.8 V vs NHE. Both linear and bridged adsorbed CO molecules were detected. The linear CO disappeared at –0.8 V vs NHE. Since the reduction of adsorbed CO proceeded at cathode potentials less than –1.0 V vs NHE, the bridged type CO was presumed to be the electroactive species. It can be concluded that Ni cathodes had favourable electrocatalytic properties for C_1–C_4 paraffin formation (CH_4, C_2H_6, C_3H_8, *n*- and *i*-butane). By contrast, on copper CH_4 and C_2H_4 were selectively produced [12, 47, 65, 146–151].

Bandi and coworkers [6] performed high pressure electrolyses at platinum cathodes in the presence of tetraalkylammonium salts, both in aqueous solutions and in supercritical CO_2.

3.1.2. Fe, Ru and Os electrodes. Iron cathodes have been widely examined for their use in CO_2 electroreduction. Hori and coworkers [47] found that Fe cathodes readily formed hydrogen in neutral and mildly acidic solutions and this product was dominant by far. Nevertheless, Frese and Canfield [101] obtained significant amounts of CO on Fe electrodes. In 1995, Hara and coworkers [73] reported, in high pressure (30 atm) experiments on Fe electrodes, formic acid as the main product, methane as the byproduct and traces of ethane and ethylene, as side-products. The faradaic yield was, however, unsatisfactory, about half of the current being consumed on hydrogen evolution. In another series of experiments at high pressure and large current density (120 mA cm^{-2}) the same authors [152] achieved 60% efficiency for HCOOH formation. Long-chain hydrocarbons such as 1-butene, trans-2-butene iso and *n*-pentanes formed as byproducts, with a maximum partial current density of approximately 10 mA cm^{-2}.

Ruthenium was the first metal found to catalyze the electrochemical methanation of CO_2 [106–108]. In other experiments with Ru cathodes methanol (r_f = 25%) and CH_4 (r_f = 30%) were formed [109]. The presence of carbon and CO among the reduction products were explained by two-electron reduction processes as described by Equations 22 and 23:

$$CO_2 + H_2O + 2e^- \longrightarrow CO + 2OH^- \quad (22)$$

$$CO + H_2O + 2e^- \longrightarrow C + 2OH^- \quad (23)$$

Metallic osmium cathodes (operated at –0.69 V vs SCE and at low current density) were selective for CH_3OH formation (r_f = 57%), and only traces of CO were obtained (r_f = 0.11%) [101]. However, on carbon electrodes electroplated with osmium the formation of methanol ceased.

3.1.3. Co, Rh and Ir electrodes. Cobalt electrodes yielded mainly CO ($r_f \leq 26\%$, in slightly acidic sodium sulfate or neutral $LiHCO_3$ solution at 333 K) [101]. Usually almost no reduction occurred on Rh and Co electrodes. When used at ambient pressure, the predominant product was H_2 from water reduction [73]. By contrast, at 30 atm pressure and elevated current densities (163–700 mA cm^{-2}), CO and HCOOH were obtained in addition to hydrogen. Under similar conditions Rh electrodes yielded mainly CO (61.0%) and HCOOH (19.5%). Iridium electrodes decomposed water to H_2 (48.3%), and only limited amounts of HCOOH (22.3%) and CO (17.5%) were produced [73].

3.1.4. Cr, Mo and W electrodes. Molybdenum electrodes were investigated by Summers and Frese [153], since these metals were among the first to show electrocatalytic activity for CH_3OH formation. In fact, a Mo electrode is a metal/metal oxide system. When a CO_2 saturated sodium sulfate solution (pH 4.2) was electrolyzed at –0.7 to –0.8 V vs SCE (at room temperature), methanol was the main product (r_f = 50–100%). In dilute H_2SO_4 the methanol yields were in the range of 20 to 46%. Carbon monoxide (1 to 20%) and CH_4 (0.1 to 3%) were the byproducts. By scanning the electrode potential from +0.2 to −1.2 V vs SCE the rate of methanol formation was enhanced. A two-step reaction mechanism was assumed, which involved the participation of Mo (Equations 26 and 27):

$$2CO_2 + 3Mo + 4H_2O \longrightarrow 2CH_3OH + 3MoO_2 \quad (26)$$

$$3MoO_2 + 12H^+ + 12e^- \longrightarrow 3Mo + 6H_2O \quad (27)$$

In CO_2 electroreductions at Mo cathodes in PrC, DMSO and AN, oxalic acid was obtained with current efficiencies in the range of 20–35%, while 5–30% CO formed as the byproduct [12].

Tungsten electrodes operated at low current densities ($32\,\mu A\,cm^{-2}$), at 333 K, in Na_2SO_4 solution (pH 4), produced CH_3OH (r_f = 76%) and CO (22%) [101]. In high pressure electrolysis experiments on W, Hara and coworkers [73] obtained 31.9% oxalic acid as the main carbon-containing product, along with 53.1% H_2. On chromium electrodes, mainly H_2 was evolved, with CO (r_f = 6.2%) being the only CO_2 reduction product [99]. At increased pressures (30 atm) about 20% of the electricity produced carbon-based products (11.8% CO and 8.2% HCOOH) [73].

3.1.5. Ti, Zr, Nb, Ta and Mn electrodes. There are only a few accounts of experimental work on CO_2 electroreduction on Ti, Zr, Nb and Ta electrodes. At 30 atm all four metals produced a small amount of HCOOH (3.5–7.6%), and significant amounts of H_2 [73]. However, on Zr, carbon monoxide generation was also notable (32.5%). The same authors found that on Mn electrodes, operated at 30 atm, 78.8% H_2 evolved, and only 6.5 of the CO_2 was reduced (2.8% CO and 2.8% HCOOH formed) [73].

3.2. *Experiments performed in nonaqueous media*

Vassiliev and coworkers [99] electroreduced CO_2 on Pt in non-aqueous supporting electrolytes. As a result, CO and CO_3^{2-} were obtained, according to the mechanism proposed by Haynes and Sawyer [98] (Equations 24 and 25):

$$(CO_2)_{ad} + e^- \longrightarrow (CO_2^- \cdot)_{ad} \tag{24}$$

$$2(CO_2^- \cdot)_{ad} \longrightarrow CO + CO_3^{2-} \tag{25}$$

Nickel and platinum electrodes in TEAP/PrC electrolyte formed CO and HCOOH (in a ratio from 6:1 to 8:1, wt/wt) at –2.8 V vs Ag/AgCl. Traces of oxalic acid [12] were also detected. In similar experiments performed on Pd electrodes, significant amounts of oxalic acid (CO/HOOC — COOH = 2:1, wt/wt) and only traces of formic acid were observed [12].

Iron cathodes have proven excellent for the selective preparation of oxalic acid. When used in TEAP/PrC; the HOOC-COOH/CO/H_2 product ratio was approximately 3:1:2 [12]. In DMSO and AN, the r_f of oxalic acid was significant (r_f = 50–60%).

Several metals that had been previously found inactive in aqueous CO_2 electroreductions have shown, however, some electrocatalytic activity in nonaqueous media [12]. Dimerization of the $CO_2^- \cdot$ anion radical to oxalate ions is prevalent in nonaqueous supporting electrolytes (TEAP/PrC). For electroreductions performed on Ti, Nb and Cr electrodes the reaction proceeded according to the mechanism shown in Equations 28–30. The dinegative oxalate ion formed by the dimerization of the $CO_2^- \cdot$ radical (Equation 28) may undergo further reduction to glyoxalate (Equation 29), and eventually to glycolate anions (Equation 30).

$$2(CO_2^- \cdot)_{ad} \longrightarrow {}^-OOC - COO^- \tag{28}$$

$$\begin{aligned} &{}^-OOC - COO^- + 2H^+ + 2e^- \\ &\longrightarrow {}^-OOC - CHO + OH^- \end{aligned} \tag{29}$$

$${}^-OOC - CHO + 2H^+ + 2e^- \longrightarrow {}^-OOC - CH_2OH \tag{30}$$

No glyoxalic acid was obtained on Mo electrodes; the reaction advanced only to oxalate [12].

4. Possible technological use of CO_2 electroreduction

In a recent review paper Ayers [5] gave an excellent discussion of the energy requirements for CO_2 electroreduction relative to the catalytic reduction procedure. The author stressed that energy requirements are critical for the technological acceptance of the process. If the anodic reaction is water oxidation, the magnitude of the cell voltage is about 3 V, much higher than the energy requirement for water electrolysis [5]. To render the electroreduction process efficient, high throughput gas diffusion electrodes are needed. The capital costs for such reactors are significantly greater than those needed for the heterogeneous catalytic reduction of CO_2 in packed bed catalytic reactors. However, the much greater specific reaction rates and the versatility of the electrochemical system for obtaining various products argue for the usefulness of electrochemical reduction as a means for carbon dioxide reduction/elimination.

5. Conclusions

It has been shown that the products of the electrochemical CO_2 reduction depend on the electrocatalytic activity of the cathodic metal. A large number of examples have been provided to stress the different electrocatalytic activity displayed by electrodes made of sp and of d group metals, respectively. Their dissimilar behaviour formed the criterium of the cathode classification proposed in this paper. Of great importance are the composition of the supporting electrolyte (aqueous or nonaqueous solutions), and the experimental parameters (cathode potential, current density, temperature and pressure), as well. Spectacular faradaic efficiencies for HCOOH and oxalic acid have been achieved in high pressure experiments at sp group metal electrodes with high overpotential for hydrogen evolution such as Pb, Hg and In. Indium, known for its noteworthy selectivity in the synthesis of formic acid at ambient pressure, has recently been used in high-pressure experiments [154]. At 60 atm in aqueous $KHCO_3$ solution HCOOH was obtained at current densities useful for technological applications ($560\,mA\,cm^{-2}$). Mercury and graphite showed different electrocatalytic activities when used in aqueous quaternary ammonium salt supporting electrolytes. However, the major product for both electrodes were acids: oxalic acid and malic acid. The electroreduction of CO_2 on metals of the 8th group yielded in various active intermediates, which were able to form valuable products in subsequent processes. Typically, formate ions and hydrocarbon molecules formed on palladium, while the main products on ruthenium were methanol and methane. Copper cathodes are among the most promising options for hydrocarbon manufacturing. As the current efficiency for methane and ethane depends on the continuous removal of the products from the electrode surface, the use of rotating disc electrodes is recommended (vibrating electrodes may be the technical solution at the industrial scale). The main electroreduction products obtained on sp and d group metal cathodes in aqueous and nonaqueous supporting electrolytes are systematized in Fig. 4. It should be noticed that there are a very few intercrossings between the four quarters of the scheme, that is, similar reduction products are formed by each of the four groups of electrodes (sp group metals in aqueous and nonaqueous electrolytes, and d group metals in aqueous and nonaqueous electrolytes, respectively). This demonstrates that each group is consistent, and supports the classification criterium used in this paper. This classification system represents an alternative strategy in evaluating the domain of CO_2 electroreduction. The approach is in many respects better than the previously used empirical ones, where no connections were made between the nature of different cathode metals that yield identical electroreduction products. Thus, the sp–d group metals pair combined with the aqueous /nonaqueous supporting electrolyte couple can provide a feasible and useful classification criterium.

The large number of mechanisms proposed for the electroreduction of carbon dioxide indicates that this topic has still not been elucidated. Sophisticated mechanistic studies are currently being performed. Examples include FTIR monitoring of the electroreduction process in nonaqueous solution [155], study of the poisoning of the electrode surface and the role of surface and subsurface hydrogen by isotopic product distribution [156], and investigation of the adsorption and electroreduction of CO_2 on Cu(1 0 0), Cu(1 1 0) and Cu(1 1 1) [157] and on rhodium single crystal electrodes [158], respectively. The electrochemistry of CO_2 is a continuously growing field. Novel procedures and even new reduction products are being reported. A recent example is the high current density electroreduction of carbon dioxide on copper cathodes in CO_2–methanol solution [103, 159]. At sufficiently elevated pressure the mole fraction of CO_2 can be as high as 0.94. The electroreduction of such concentrated CO_2 solution can be considered as the electrochemical reduction of *liquid* CO_2 [103]. Gold electrodes have been recently introduced for analytical purposes [160, 161], namely for the development of a new microelectrode CO_2 sensor. In the described application CO_2 is being electrochemically reduced at unshielded gold microdisc electrodes in DMSO in a standard reaction cell. Shibata and coworkers [162] obtained urea by the simultaneous reduction of CO_2 with nitrate and nitrite ions. In the procedure proposed by the authors copper-loaded gas diffusion electrodes were used in aqueous $KHCO_3$ supporting electrolyte, to which arbitrary concentrations of KNO_3 or KNO_2 were added.

Several recent papers related to the electrochemistry of CO_2 are of technological interest [163–168]. Copper tube electrodes have been employed for the production of methanol and formic acid [163], and the mechanism of the electrochemical mass

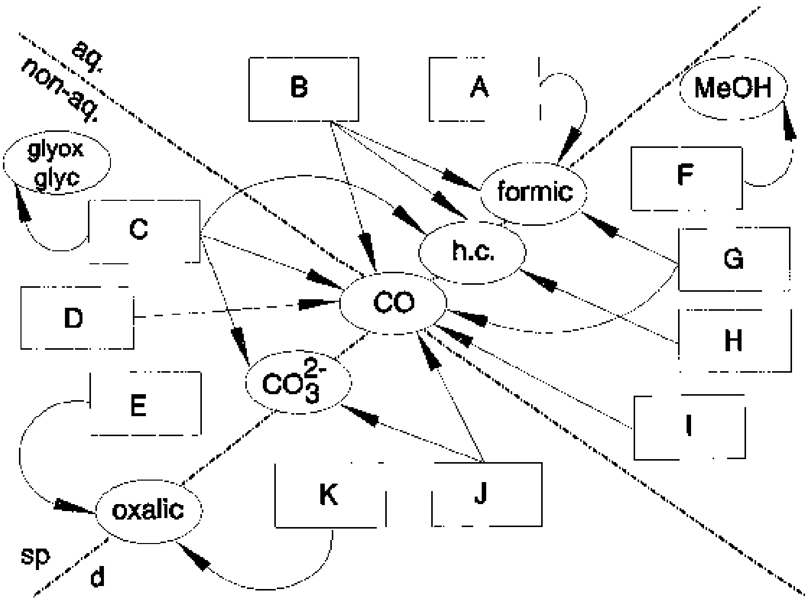


Fig. 4. Classification of the procedures of CO_2 electroreduction based upon the nature of the cathode material (sp or d group metals) and the solvent used for the supporting electrolyte (aqueous or nonaqueous solutions).(A) Cu, Zn, Sn; (B) In, C, Si, Sn, Pb, Bi, Cu, Zn, Cd, Hg; (C) In, Sn, Pb, Cu, Au, Zn, Cd; (D) In, Sn, Au, Hg; (E) In, Tl, Sn, Pd, Zn, Hg; (F) Mo, W, Ru, Os, Pd, Pt; (G) Ni, Pd, Rh, Ir; (H) Fe, Ru, Ni, Pd, Pt; (I) Zr, Cr, Mn, Fe, Co, Rh, Ir; (J) Ni, Pt; (K) Ti, Nb, Cr, Mo, Fe, Pd. The products were formic acid (formic), hydrocarbons (h.c.): methane, ethane, ethylene, propane, *n*- and *i*-butane; oxalic acid (oxalic); glyoxylic acid (glyox); glycolic acid (glyc); methanol (MeOH) along with superior alcohols (ethanol,*i*-propanol); aqueous solution (aq.); nonaqueous supporting electrolyte (non-aq.).

reduction of CO_2 to alkanes and ethanol was studied by means of Cu-loaded gas diffusion electrodes [164]. Additional electrodes are explored in high-pressure experiments [165] for obtaining formic acid with elevated faradaic yields (~100% on In, 92% on Sn and 91.2 on Pb electrodes). Attention is paid to the kinetics of the electrochemical reduction of carbon dioxide [166]. Studies that may contribute to the application of CO_2 electroreduction at the preparative scale include the measurement of the diffusion coefficient of carbon dioxide in high pressure water [167], new developments in CO_2 storage technology [168], solubility studies in organic solvents [95]. The increasing number of patents in this field [69, 112, 123–125, 169] support the conclusion that the electroreduction of carbon dioxide at the industrial scale is no longer an unrealistic dream, but has promising chances of being achieved in the near future, provided that relatively inexpensive electricity is available.

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