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Effects of process conditions and electrode material on reaction pathways for carbon dioxide electroreduction with particular reference to formate formation

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Abstract

This paper reviews the most common reaction pathways for CO_2 electroreduction proposed by various workers in recent years. Each pathway involves certain intermediate compounds and certain end products and thus the pathways promoted, within a specific process, can be deduced from which of these have been detected. There are considered to be four principal pathways, each based on one of the following reactions: (1) CO(g) formation via disproportionation, (2) $\bullet CO_2^-$ radical formation, (3) COOH(ad) formation and (4) the formation of reduced CO_x^{y-}(ad) species giving a range of reduced CO_2 end products. This paper places particular emphasis on the formation of HCOOH. The effects of electrocatalyst and process conditions on reaction pathways is also reviewed.

1. Introduction

The reduction of global CO_2 emissions is currently an issue of major importance [1, 2]. This has stimulated research into the development of economic electrochemical processes for the removal of CO_2 from effluent streams. Such processes would be of particular interest if useful end products could be produced, if other effluent streams could also be used as reactants or if such a process could be electrogenerative. All of these scenarios may be possible in the future [3]. An essential part of the development of such processes is a sound understanding of the possible electroreduction pathways for CO_2, and how these pathways may be promoted or inhibited.

This paper reviews research undertaken by a variety of workers, and presents a diagram (Figure 1) showing four principal pathways: (1) a reaction between CO_2^-(ad) and CO_2(g) giving CO(g) through disproportionation; (2) a formation of a $\bullet CO_2^-$ radical, with the end product dependent upon the nature of the electrolyte; (3) a formation of a $\bullet$COOH(ad) species, with a formate structure leading to a yield of formate; and (4) a formation of a range of adsorbed reduced CO_2 (i.e., CO_x^{y-}) species, giving yields of CO, hydrocarbons and alcohols. The studies reviewed include those that focus primarily on intermediate adsorbed species, end products, and the electrocatalytic nature of cathodes constructed from a variety of metals. Particular reference is made to the formation of HCOOH, this being a product for which there is a growing demand and which is currently made by processes that are neither straightforward nor environmentally friendly. HCOOH can be produced with a higher selectivity than other end products, and workers who claim to have developed an electrogenerative process produced HCOOH as their end product, [3–6].

Consideration of the pathways promoted by a particular cathode (taking into account the process conditions) allows inferences to be made as to the tendency of that cathode to adsorb and desorb various key species. Thus a reaction scheme is proposed in which reaction products are shown as an end result of these adsorption/desorption properties (Figure 3). For the above, principal pathways 4 and 3 will be dominant if the cathode has a pronounced tendency to retain CO_x^{y-} species. Pathway 4 will be preferred to pathway 3 if the H(ad) cathode coverage is low relative to the availability of H^+ ions. This would include cathodes with a low tendency to adsorb H(ad), and also low pH systems. Any system in which H(ad) dominates over CO_x^{y-} (ad) species will give predominantly H_2 evolution at the cathode.

The effects of conditions such as temperature, pressure, pH and applied potential can be superimposed onto the reaction scheme. This means that if the adsorption and desorption properties of the cathode have been established under one set of conditions, then the effects of changing the process conditions can be qualitatively predicted. Thus it should be possible to use theoretical predictions to assist the fine-tuning of operating conditions to give the optimum yield of a desired end product. This paper suggests that increasing temperature will preferentially promote pathways 1 and 2, and increasing the CO_2 partial pressure, P_{CO_2}, will promote the retention of CO_x^{y-} species and suppress H_2

evolution. The findings of recent workers suggest that a reduction in pH will increase the H(ad) coverage which, in some systems, will increase H_2 evolution and reduce CO_2 reduction. In systems which promote pathway 4, however, increasing the availability of protons will enhance the production of highly reduced CO_x^{y-} species. Similar findings exist for applied potential, with the product profile changing with applied potential. The maximum applied potential before H_2 evolution becomes dominant is greater for a system with a high retention for CO_x^{y-}(ad).

Finally, the paper considers the cathode properties in terms of the electron configuration of the metal catalysts present within the cathode. Research indicates that (with a few exceptions) the adsorption/desorption properties of a cathode can be predicted from these electron configurations. This allows predictions to be made as to which metal groups are likely to produce the best yield of a particular end product under a given set of operating conditions. The metals which have been found to most effectively catalyse CO_2 reduction are those with a small number of electrons in the sp orbital and/or full d-orbitals. Examples of these include In, Pb, Cu and Pd.

This review brings together ideas on theoretical pathways and actual performance, with the objective of aiding the construction and fine tuning of industrially useful processes.

2. Electroreduction pathways CO_2

There has long been an interest in the electroreduction of CO_2 in order to make carbon based compounds, and there have been parallels drawn between this and photosynthesis. In their review of the topic Jitaru et al. [7] refer to papers which review over 100 years of work on the subject. The review concludes that CO_2 represents an infinite source of carbon that can be generated into methanol, ethanol, aldehydes, methane, ethylene, formic and oxalic acids. An alternative option is to develop a process that will produce a useful ratio of CO to H_2 (i.e., Syngas). The growing promise of electrochemical methods is leading to many papers and patents. Much work is also ongoing on photocatalytic reduction [8–12].

Carbon dioxide can be reduced to a wide range of end products [13]. Each of these paths from CO_2 to a particular product can be described as one of many competing 'overall' reactions. The extent to which each progresses will depend on the metal catalyst, the electrolyte and the cathode potential. Each overall reaction has its own open circuit potential and, for any given system, its own 'overpotential against current density' profile. Overall reactions are, however, a series of intermediate steps with competing reactions at each of these steps. It is possible therefore that an overall reaction with a very positive open circuit potential, may not occur to a significant extent within a particular system. This will be the case if one of the intermediate steps does not occur to a significant extent, there being a more favoured alternative reaction at that point.

Some of the common reduction products are shown in Table 1. The equilibrium potentials of each reaction have been compared by Sullivan et al. [13] under standard conditions against NHE. As indicated previously, the actual extent to which reaction occurs will depend (notwithstanding their $E°$ values) on the condi-

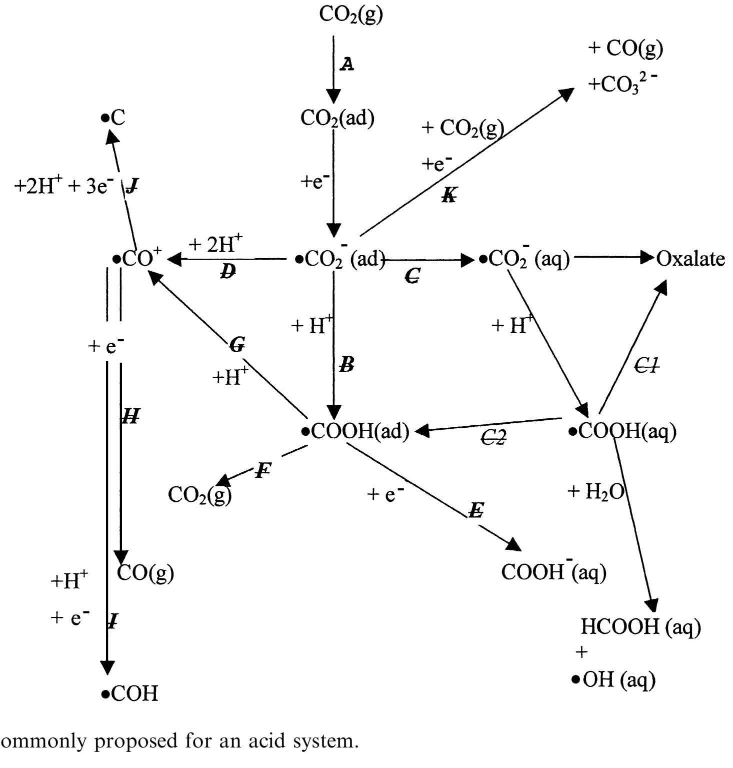


Fig. 1. CO_2 reduction routes commonly proposed for an acid system.

Table 1. Equilibrium potentials for various CO_2 electroreduction reactions, 298 K

	$E°$/V
$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	−0.475
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.199
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.109
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.071
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	+0.030
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	+0.169

tions of the particular system. Sullivan et al. [13] also cite the importance of pH and give the potential for the HCOOH reaction as improving to E=−0.15 V as pH tends to 0.

The competing intermediate reactions and resulting products can be most easily shown in a branching form. At each point, competing reactions create different branches. Eventually end products can be grouped together according to what intermediate species they have in common. In Figure 1, each competing reaction is given a reference letter and is then described in more detail in the following sections. Many of the reaction paths are described in differing ways by different workers, for example, path *B* is frequently described as being a reaction between $\bullet CO_{2\,ad}^-$ and either H_{ad} or H_2O_{ad}. Most of the reactions shown in Figure 1 are proposed by Sullivan et al. [13], and assume a high availability of protons.

2.1. *Reaction path A: the adsorption of CO_2 onto the electrode surface*

Path *A* has been suggested by some workers [13] to be prerequisite to any significant CO_2 reduction taking place. In liquid electrolytes there may be an intermediate reaction whereby the CO_2 forms a complex within the electrolyte, for example in an aqueous system the first reaction may be

$$CO_2(g) \longrightarrow CO_2(aq).$$

Alternatively, it has been suggested that, in aqueous solution, the equivalent of paths *A* and *B* shown in Figure 1, could take place via the following radicals:

$$CO_2(g) + e^- \longrightarrow CO_2^-(g)$$

followed by

$$\bullet CO_2^-(g) + H_2O \longrightarrow \bullet COOH(ad) + OH^-$$

Another possibility is reaction with a species within the electrolyte (heterogeneous electrocatalyst) that will reduce the CO_2 away from the electrode surface (and be regenerated by its own subsequent reaction at the electrode). If an aqueous system requires an intermediate hydration step before adsorption occurs, then the CO_2(ad) concentration at electrode sites will be limited by the solubility of CO_2 in water, which is 0.033 mol l^{-1} at standard temperature and pressure. Also the species CO_2(aq) reacts to give HCO_3^- and CO_3^{2-} ions, especially in alkaline solution. Use of gas diffusion electrodes (GDEs) supposedly overcomes limitations arising from relatively low CO_2(aq) availability, by allowing the formation of CO_2(ad) directly from the gaseous state.

If the catalyst metal is given the symbol M, then the adsorbed species can be represented as M—CO_2. One of the functions of the catalyst is to reduce the activation energy required to ionize the CO_2 species. The formation of a species M—CO_2^- may be a simple adsorption:

$$M + CO_2 + e^- \longrightarrow M{-}CO_2^-$$

or, it may be a displacement of the form:

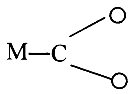
$$M{-}H + CO_2 \longrightarrow M{-}CO_2^- + H^+$$

(possibly catalysed by high pH)

A minority of workers dispute the existence of an M—CO_2 species for some systems [14]. The orientation of the M—CO_2 species and the charge density distribution will depend on the metal involved and this will govern the subsequent reactions. The following possibilities exist [13]:

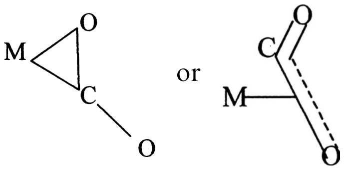
(a) an η^1 bond through an oxygen atom, that is, M—O=C=O. **Not** found.

(b) an η^1 bond through the carbon atom, that is,



Metals promoting this type of bond include Fe, Co, Rh, W, Ir (groups 4 to 8 giving a carboxylate).

(c) an η^2 bond between the carbon and oxygen, that is,



Examples of metals promoting the η^2 bond are Ni, Nb and Mo.

The M—CO_2 species may undergo different reactions, for example:

$$M{-}CO_2 + Y \longrightarrow MY + CO_2$$

This reaction type does not favour reduction products.

$$M{-}CO_2 \longrightarrow M^+ + \bullet CO_2^-(aq)$$

The oxidation of M favours formate production in aqueous electrolyte or the oxalate (reaction path *C*) in aprotic electrolyte.

In the presence of protons, the M—CO_2 species can undergo protonation or electrophilic attack (reaction path Ƀ or Đ). The metal surface must interact with a CO_2 species in preference to a M—H bond, (or allow a substitution) otherwise the predominant product at the electrode will be hydrogen. The availability of protons and the H_{ad} coverage on the electrode will have a strong influence on these reactions.

2.2. *Reaction path Ƀ - protonation of CO_2 to form MOCOH*

The protonation reaction can be represented by

$$\mathrm{M{-}CO_2 + e^- + H^+ \longrightarrow MOCOH}$$

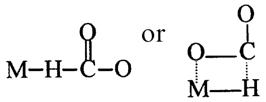
but a number of possibilities are possible, including the following:

(i) *substitution*, where the CO_2 molecule is interposed between an existing M—H bond.

$$\mathrm{M{-}H + CO_2 \longrightarrow MOCOH}$$

(ii) *reaction* between M—CO_2^- and H_2O_{ad} or H_{ad}

The first reaction (i) is proposed for Pd electrodes as an alternative to the formation of M—CO_2 [13, 14]. Such a substitution would not occur for a system where the M—H bond was very strong. A metal promoting this reaction will have a slightly basic nature, the charge distribution on the M—H complex becoming $M^{\delta+}$–$H^{\delta-}$, this being an appropriate distribution to promote reaction with the $C^{\delta+}O_2^{\delta-}$ to give the following complexes:



An alternative to a simple metal would be a complex with a ligand withdrawing electron density from the metal centre, that is, $L^{\delta-}$—M—$H^{\delta+}$, such as described by Caix et al. [15].

Jitaru et al. [7] propose that an electrode with a good bond strength for both M—CO_2 and M—CO_2^- may promote a reaction with either a neighbouring M—H species, in the case of electrodes catalysed by d-group metals, or with M—H_2O for sp-group metals. It can be predicted that a system that gave formate mainly via the reaction between MCO_2^- and H^+ would perform best under highly acidic conditions. Any system that gives a good yield of formate at high pH is either following one of these alternative routes to MOCOH or is releasing a CO_2^- radical as per path Ȼ.

2.3. *Reaction path Ȼ: CO_2^- radical released into the electrolyte*

An electrode surface which adsorbes CO_2 but readily releases CO_2^- would favour path Ȼ and give the species •CO_2^-(aq) (or a •CO_2^- electrolyte complex for a nonaqueous system) [16]. This path might be blocked by very low pH which may promote paths Ƀ and Đ instead. The •CO_2^-(aq) species can react with H_2O/H^+ in the electrolyte and produce the •COOH radical [16–18]. This can either be readsorbed to the electrode surface (path Ȼ2) or react further with water to give HCOOH (aq) plus an •OH radical [18, 16]. Any •COOH radicals present in nonaqueous systems can undergo a dimerization reaction to $H_2C_2O_4$ (path Ȼ1). In one system, where a high yield of formate was obtained, spectroscopic studies showed MCO_2^- to be the only adsorbed species and it was concluded that path Ȼ was the dominant reaction [16].

In a QAS system the oxalate is formed by the dimerization of •CO_2^- [7, 17, 19, 20], while in a nonaqueous system it is thought to be [16, 21] via the reactions

$$\mathrm{CO_2 + CO_2^- \rightarrow {\bullet}(CO_2)_2^-}$$

Presumably the QAS system will facilitate the release of a solvated •CO_2^- species more readily than a nonaqueous system.

2.4. *Reaction path Đ: removal of 'O' from the M—CO_2^- species*

The electrophilic attack on the M—CO_2 species can be represented by

$$\mathrm{M{-}CO_2^- + H_2O \longrightarrow MCO^+ + 2\,OH^-}$$

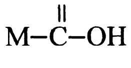
or, perhaps more correctly, by

$$\mathrm{M{-}CO_2^- + 2H^+ \longrightarrow MCO^+ + 2\,H_2O}$$

In effect a proton has removed one of the oxygen atoms, instead of becoming attached to it. This is favoured when M has a basic nature. (an 'oxophylic complex' could be used in place of protons). Paths Đ and Ǥ both involve the withdrawal of electron density from the metallic centre and the separation of an OH^- group from the adsorbed complex (i.e., nucleophilic elimination). These paths occur in systems with Cu catalysed electrodes, although the pathways are blocked by high pH.

2.5. *Reaction paths Ɇ, Ꞙ, Ǥ: reaction of species COOH(ad)*

The M—OCOH species is formed by the protonation reaction in the carboxylic form:



$$\mathrm{M{-}C({=}O){-}OH}$$

Unless stabilized, it will tend to decompose back to M—H + CO_2 or undergo a nucleophilic attack, losing an OH^- and giving M—C=O^+, according to the following:

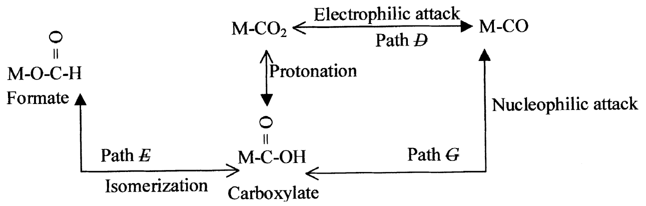
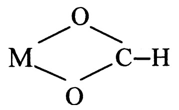


Fig. 2. Reactions of carboxylate/formate isomers (after Sullivan et al. [13]).

$$M—COOH + H^+ \longrightarrow M—CO^+ + H_2O$$

Selection of appropriate metal catalysts, however, allows stabilization and results in isomerization to the formate form. These reactions are summarized in Figure 2 (based on Sullivan [13]).

It has also been suggested that the intermediate species



may be present [13], for example, where M represents certain Ru complexes.

It is from the adsorbed formate isomer that the release of HCOOH will occur. This may be via the reaction

$$\bullet COOH + e^- \longrightarrow COOH^-(ad) \longrightarrow COOH^-(aq)$$

Alternatively, the release may come via a hydrated form

$$\bullet COOH + e^- + H_2O \longrightarrow C(OH)_2 + OH^-$$

and

$$C(OH)_2 \longrightarrow HCOOH$$

The dissociation of HCOOH to H^+ $COOH^-$ will be greater under alkaline conditions.

The production of an M—CO intermediate via routes *D* or *G*, is thought to be common for Cu and Ru and some other d group metal catalysed electrodes. It is generally believed to be present in systems which produce highly reduced products such as CH_4, C_2H_4 and CH_3OH. It has been detected by a number of workers, [22, 23]. Hori et al. [24] proposed Cu—CO as an intermediate when they produced the same end products starting with both CO_2 and CO. Some workers have found such routes to be blocked by either increasing pH [13, 25, 17] or by increasing operating pressure [26].

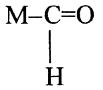
From Figure 1 it can be seen that increased pH is likely to block routes *D* and *G*, whilst leaving route *B*, to •COOH(ad), less effected or unaffected if the route is actually through the reaction with H_{ad}, as suggested by Jitaru et al. [7]. Similarly, an increase in pressure may increase M—H but not H^+. Thus pH and pressure increases promote route *B*, giving the formate, over the routes giving CO_{ad}.

Since the formation of the MCO (carbonyl) group is dependent on the transfer of electrons to a departing OH^- group, it is unsurprizing that the peak yield of highly reduced products usually occurs at a more negative potential than the peak yield of HCOOH [17].

2.6. *Reactions H, I, J: further reduction reactions*

These reaction paths are generally considered to be associated with Cu, Ru and d-group metal catalysed cathodes [13, 24, 17, 27, 28]. From the species M—C=O$^+$, the addition of one further electron may lead to the release of CO(g) (reaction path *H*). The peak production occurs at a greater applied potential compared to HCOOH and an increase in pressure generally promotes HCOOH more than CO formed via this route. The stability of M—CO is seen to be a barrier by some workers [24, 29] who found that when CO gas was used the system tended to deactivate.

In reaction path *I*, the addition of a proton and an electron to M—C=O$^+$ yields the following species:



$$\underset{\displaystyle H}{\overset{}{M\text{–}\underset{|}{C}\text{=}O}}$$

From this the group of products CH_2CO, CH_3CHO, C_2H_5OH, C_2H_4,C_2H_6 and C_3H_7OH can be formed. Sullivan et al. [13] also indicate that the species will undergo isomerization to the form M=C—O—H, to give the species CH_3OH. This last reaction appears to be favoured by Ru more than by Cu [29]. Kyriacou and Anagnostopoulos used Cu electrodes to show a yield of CO (path *H*) increasing with electrolysis time at the expense of the yield of C_2H_4 (path *I*) [30].

In reaction path *J*, the addition of three electrons and two protons to M—C=O$^+$ results in the removal of the oxygen atom to form a •C species, which subsequently reacts with further protons and electrons to give C_2H_2 and CH_4. Given that the electrodes are normally carbon based, some workers have been able to demonstrate that the •C species is always from the original CO_2 and never from the carbon of the electrode. One study of the reaction producing CH_4 found the •COOH intermediate, but not a •CO intermediate, and suggested that there may be an alternative route other than via •CO. Sullivan et al. [13] described a possible route where MCOH could be formed from MCOOH. Systems which promote M—C formation can be deactivated, especially at elevated temperatures, and a build-up of carbon may be found on the electrode [13, 29]. Lee and Tak have investigated a way to minimize this by modulating the applied potential [31]. Others have also tried this approach [32].

Path *J* is promoted by low temperature [17] and can be seen to be in competition with route *I*; for example, as the CH_4 yield rises the yield of C_2H_4 falls and vice versa. Summers and Frese [29], produced CH_4 from CO_2, CO, and CH_3OH. In each case they believed MC to be a common intermediate. Both Cu and Ru are believed to have a low tendency for the formation of M—H, and it is notable that catalysts that promote path *J* have a lower optimum operating pH than other catalysts [29].

2.7. *Reaction path K: disproportionation*

This reaction path gives rise to CO_3^{2-} ions, the presence of which is not necessarily proof that such a reaction is occurring. Ito and Ikeda [33] considered this reaction common in nonaqueous systems. The proposed reaction [13, 34] is that incoming CO_2 reacts with MCO_2^-, which acts as an O acceptor.

The reaction can be distinguished from reaction path *H* in three separate ways:

(i) The catalysts that promote it are s and sp group metals, typically Ag and Au. The reaction path *H* is usually promoted by d group metals.

(ii) The peak applied potential is usually less than that for HCOOH production [33]. The peak for path *H* is usually at a greater applied potential than for HCOOH production.

(iii) Increasing operating pressure does not decrease the yield of CO via disproportionation relative to HCOOH [26] and reducing the operating pH is not likely to increase the yield. In contrast, path *H* is usually blocked by increased P_{CO_2} and promoted by reduced pH.

Hirota et al. [35] have had some success with a photoelectroreduction process using a *p*-InP cathode. The main product was CO, which was formed via a dimerized CO_2 anion radical. This type of intermediate species is likely to exist for most disproportionation reactions, and has been identified as an intermediate species by a number of workers, such as [8, 36].

2.8. *Dependence of reaction paths on the electrode adsorption properties*

Simplistically, the reaction paths *A* to *K* may be displayed in flow chart form as a function of the

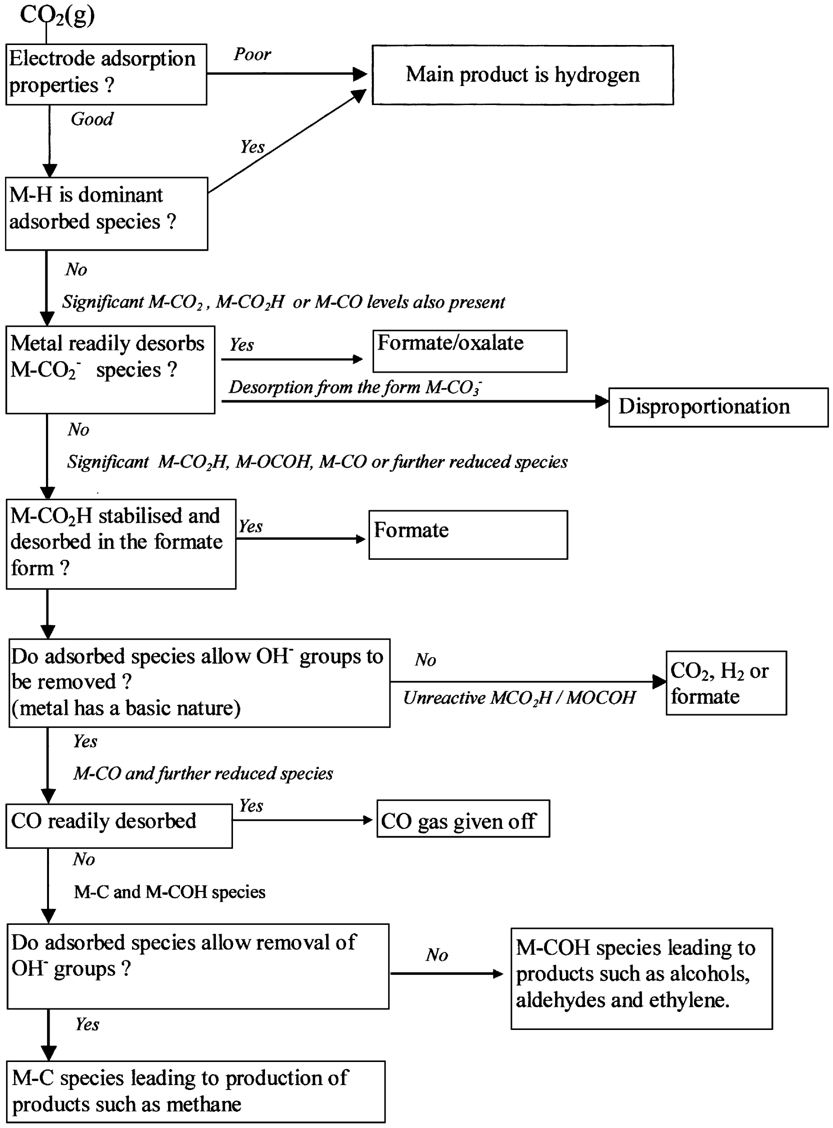


Fig. 3. Reaction paths as a function of electrode adsorption properties.

electrode CO_2 adsorption/desorption properties. This is illustrated in Figure 3.

3. Adsorption and desorption reactions contributing to the reduction of CO_2 to HCOOH

In Section 2 it was indicated that HCOOH can potentially be produced from two of the four principal pathways for CO_2 reduction. Those pathways have been proposed by a number of workers but notably drawn together by Sullivan et al. [13]. HCOOH can be produced following the formation of $\bullet CO_2^-$, that is, reaction paths *A*/*C*, and also following the formation of COOH(ad), (i.e., reaction paths *A*/*B*). Sections 3 and 4 consider in more detail the range of possible adsorbed intermediates that may exist and how process conditions and selection of electrocatalysts may affect their formation.

Udupa et al. [18] and Aylmer-Kelly et al. [16], proposed that a $CO_2^-(aq)$ species can be formed, which reacts with water to form a •COOH(aq) species, which is then either readsorbed at the electrode, or reacts with another water molecule to give HCOOH + •OH. Aylmer-Kelly et al. [16] used reflectance spectroscopy to detect the presence of $CO_2^-(aq)$ species, but found no $CO_2^-(ad)$ or COOH(ad) species. They therefore rejected pathways which involved these intermediates.

Jitaru et al. [7] review the mechanism for HCOOH formation and conclude that many workers support the idea of a COOH(ad) species being formed by the reaction between the $CO_2^-(ad)$ species and a neighbouring $H_2O(ad)$ species or neighbouring H(ad) species. Sullivan et al. [13], describe the reaction as being between $CO_2^-(ad)$ species and H^+. The conclusion that can be drawn when reviewing the different proposed reaction pathways and mechanisms, is that different pathways will be followed by different systems. Also the precise sequence of reactions that may occur within a pathway such as the conversion of $CO_2^-(ad)$ to COOH(ad) may differ from one system to another.

Previously the formation of HCOOH via COOH(ad) was shown in two steps as

$$CO_2(g) + e^- + H^+ \longrightarrow COOH(ad) \tag{1}$$

$$COOH(ad) + e^- + H^+ \longrightarrow HCOOH(aq) \tag{2}$$

but Reaction 1 may occur as any of the following sequences, depending on the electrode and process conditions:

$$CO_2(g) \longrightarrow CO_2(ad)$$

$$CO_2(ad) + e^- \longrightarrow CO_2^-(ad)$$

$$CO_2^-(ad) + H^+ \longrightarrow COOH(ad)$$

or

$$H^+(aq) + e^- \longrightarrow H(ad)$$

$$H(ad) + CO_2(g) \longrightarrow COOH(ad)$$

or

$$CO_2(g) \longrightarrow CO_2(ad)$$

$$CO_2(ad) + e^- \longrightarrow CO_2^-(ad)$$

$$CO_2^-(ad) + H(ad) \longrightarrow COOH^-(ad)$$

or

$$CO_2(g) \longrightarrow CO_2(ad)$$

$$CO_2(ad) + e^- \longrightarrow CO_2^-(ad)$$

$$CO_2^-(ad) + H_2O \longrightarrow COOH(ad) + OH^-$$

with the reaction between $CO_2^-(g)$ and H_2O being another alternative.

Alternatives to Reaction 2 include the reaction of •COOH(ad) with H_2O to give HCOOH(aq) and •OH(aq) and also the reaction of •COOH (ad) with H_2O + e^- to give a hydrated intermediate $C(OH)_2$. The number of alternatives proposed indicates that, for most systems, there will be reactions occurring in parallel. Also small changes in process conditions, electrode surface finish or electrode preparation technique may easily lead to different reaction paths becoming dominant.

Sullivan et al. [13], imply that a reaction occurring in the aqueous phase:

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$

has an $E° = +0.1$ V vs SHE. This value is significantly more positive than the value obtained when calculated from the free energy of formation using reactants at unit concentration. It should also be noted that a P_{CO_2} of 60 bar would be required to give unit concentration for $CO_2(aq)$, the solubility at 1 bar being 0.033 mol dm^{-3}. In practice the above reaction will occur at an electrode surface and involve a series of adsorption and desorption reactions. The activation energy for each adsorption and desorption depends on the electrode, the temperature and the pH. Some reactions will be spontaneous, others will require an energy input. Effective catalysis involves promoting or inhibiting the appropriate reactions, with the final products depending on which adsorbed intermediate species are formed.

Sullivan et al. [13] cite work by Hori et al. [37] and Vassiliev et al. [21] which illustrates the importance of how intermediate steps are promoted or inhibited by changing conditions and using different electrocatalysts. These workers showed a high yield of HCOOH from Hg and In electrodes, but a reaction dominated by disproportionation for a Au electrode. In aqueous solution they found the best yield at pH 5 to 6. Increased acidity promoted hydrogen evolution and increased pH increased HCO_3^- oncentration at the expense of CO_2(aq). In earlier work Udupa et al. [18] found that a pH between 7 and 9 gave the optimum yield of carbon based compounds. It may be concluded that each system has its own optimum pH.

Udupa et al. [18] found that reaction rates increased with temperature and that increased temperature appeared to decrease the yield of CH_4 in favour of C_2H_4 (using Cu electrodes). It could be argued in general that increasing the temperature is likely to reduce the yield of any products shown towards the bottom of Figure 3 and promote the yield of products (such as the oxalate and hydrogen) shown at the top of the chart. The optimum yield of formate may be obtained at a low temperature for one system and a higher one for another, depending on what reactions are competing. Theoretically, increasing temperature will favour reactions with a higher activation energy. Increased temperature may increase reaction rates and reduce overpotentials, but it may also reduce the coverage of adsorbed species on an electrode and CO_2 solubility. If there is a reasonably equal distribution of C_xO_x(ad) species versus H(ad) then the product distribution may not be sensitive to temperature. In a system where H(ad) dominates, then increasing temperature is likely to reduce the yield of carbon based products. Conversely, systems where the H(ad) is low (e.g., Ru based electrodes), may suffer deactivation from C(ad) polymerization reactions when the temperature is increased. Kaneco et al. [38] showed CO production increasing relative to H_2 production with temperature reduction, on a Ag cathode. Mizuno et al. [19] reported CO_2 reduction increasing relative to H_2 evolution with decrease in temperature.

Decreasing the pH of a system will increase the level of ‘H’ coverage on the electrode (and will affect the strength of the $M^{\delta+}$—$H^{\delta-}$ bond), but will also increase the level of CO_2(aq). Sullivan et al. [13] cite one example, where a system giving mainly CH_4 gave a reduced yield with changing pH and eventually suffered electrode deactivation due to a build up of carbon. An electrode with a low affinity for H(ad) will have a lower optimum pH for CO_2 reduction, than a system where H(ad) tends to dominate. Reduction in pH appears to increase H_2 yields in some systems (if it increases the ratio of M—H bonds to M—C bonds) but in other systems the availability of protons promotes reduction reactions.

Komatsu et al. [25] found that a cationic membrane (giving a supply of protons to a Cu cathode) gave a significant C_2H_4 yield, whereas the anionic membrane produced a better yield of HCOOH. The difference in product profile can be explained by the fact that C_2H_4 requires more protons than HCOOH during formation:

$$CO_2 + 2\,H^+ + 2\,e^- \longrightarrow HCOOH$$

$$CO_2 + 6\,H^+ + 6\,e^- \longrightarrow 1/2C_2H_2 + 2\,H_2O$$

Komatsu et al. [25] refer to other work, using Cu electrodes in $KHCO_3$ solution, which found that a higher pH favours HCOOH and a lower pH favours C_2H_4.

Sullivan et al. [13] indicate that the condition of the electrode surface can be more important than mass transport to and from the electrode, the rate of reaction being limited by surface effects. A study of the crystal orientation within a Cu electrode showed that, in some orientations, the M—CO binding was stronger, which promoted CH_3OH production, whereas in other orientations the M—C product was formed, leading to CH_4 production. These different results depended on how the surface had been prepared, [13, 39]. Studies performed with Pt and Ag crystals showed that atomically flat surfaces are less active than surfaces with step-sites when reducing CO_2 [40–43]. Similar findings were obtained when performing studies with Pd crystals [44]. All of these texts [13, 39–44] stress the importance of electrode preparation on crystal orientation and morphology of the surface. In cases where certain reaction rates are limited by surface effects, the selectivity of a system is highly dependent on these surface properties. In Section 5 several electrocatalysts are shown by different studies to give a different balance of end products even whilst operating under similar process conditions.

Hori et al. [24] worked with a Cu electrode in an aqueous system using CO instead of CO_2. Since most products formed when using Cu electrodes are all thought to include a Cu—CO complex as an intermediate step, it would be expected that the final products would be the same with CO gas as with CO_2. This did prove to be the case; however, the products did not form as readily with CO as with CO_2, which indicates a difference between the adsorption characteristics of CO compared with CO_2 gas on copper.

In some systems a deterioration in electrode performance with time is noted [31, 32, 45]. In these cases options for prolonging the electrode performance include potential modulation or pulsing [31, 32] or use of ultrasonic treatment [32].

Photoemission studies have been made to study the intermediates formed in CO_2 reduction reactions. Electrocatalysts are defined as having the function of stabilizing these intermediates and reducing the activation energy required to form them (thus reducing the overall potential of a reaction).

One example of this [13] was a system where the activation energy required for the reaction

$$CO_2(g) + e^- \longrightarrow \bullet CO_2^-(aq)$$

was found to be $183\,kJ\,mol^{-1}(-1.9\,V)$

but

$$CO_2(g) + e^- \longrightarrow \bullet CO_2^-(ad)$$

was found to be only $154\,kJ\,mol^{-1}(-1.6\,V)$

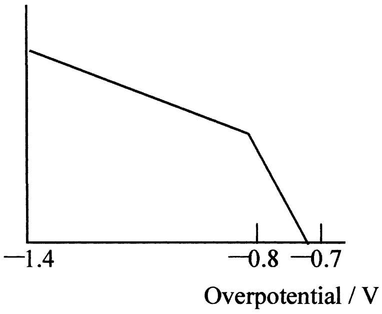


Fig. 4. Schematic of current density for CO_2 reduction against overpotential.

Sullivan et al. [13] and Vassiliev et al. [21] show that, for a number of different electrodes at various operating conditions, plots of j against overpotential frequently produce an 'elbow' shape, as shown in Figure 4. Jitaru et al. [7] also note the presence of an elbow in voltage versus current plots. In an aqueous system they propose that the first reaction step is the hydration of a CO_2 molecule followed by competition to become adsorbed onto an active site. This implies that the formation of a CO_2(ad) species is a critical limiting step within an aqueous system.

The 'elbow' shown in Figure 4 is common to most electrodes and to both aqueous and nonaqueous systems, however [21, 46]. It also occurs at approximately the same current density for these various systems. The elbow indicates that above a certain reaction rate, all the various overall reactions, giving their various end products, are being limited by the same intermediate, rate determining step. Given that this effect is even common to systems giving oxalate, by referring to Figure 1, it can be seen that the only common intermediate step requiring an energy input is

$$CO_2(ad) + e^- \rightarrow CO_2^-(ad)$$

Thus, the common occurrence of the elbow indicates that the above reaction is rate limiting, even when a variety of subsequent reactions occurs. Studies by Vassiliev et al. [21] have focused on this reaction. The potential/current density characteristic for the reaction was studied for different electrodes, pH, electrolyte, temperature and pressure. At a given potential, the current density in an aqueous system, for example, was found to be given by

$$j = kP^{\beta}_{CO_2}$$

where β took a value between 0.6 and 0.8 [21].

Hara et al. [26, 47] considered reaction mechanisms involved in CO_2 reduction to explain the benefits of increased CO_2 partial pressure. The increase increases the ratio of CO_2(ad) to H(ad) and suppresses hydrogen evolution, thereby increasing the opportunity for reaction between these adsorbed species.

Jitaru et al. [7] emphasize the importance of the ions in an electrolyte. Udupa et al. [18] cite workers who have found that the presence of HCO_3^- and CO_3^- ions enhanced formate production and who believed that formate is preferentially formed from these ions rather than CO_2 [48]. Other papers on electrogenerative formate production suggest that such ions are reactants [14, 4]. Sullivan et al. [13], however, conclude that CO_2 is the main reactant and that these ions merely enhance the reaction. Regarding cations, Jitaru et al. note that small cations such as Li^+ and Na^+ enhance CO_2 electroreduction in aqueous electrolyte systems, because they approach the cathode heavily hydrated, and are thus a source of protons, whilst not competing for sites on the cathodes. Several workers use sodium carbonate plus sodium sulphate in their electrolyte. The influence of the concentration of the supporting electrolyte on the rate of CO_2 reduction is discussed by Vassiliev et al. [21]. The use of an SPE eliminates any competition for sites on the cathode from cations (other than protons) within the electrolyte.

The study of the formation and reactions of intermediate species can be enhanced by considering the potential of intermediate species. For example, if the reaction

$$CO_2(g) + e^- \longrightarrow \bullet CO_2^-(ad)$$

has a potential of −1.6 V, and the overall reaction

$$CO_2(g) + 2\,H^+ + 2\,e^- \longrightarrow H^+COOH^-(aq)$$

has a potential of −0.199 V, then the reaction,

$$\bullet CO_2^-(ad) + 2\,H^+ + e^- \longrightarrow H^+COOH^-(aq)$$

has a potential of + 1.401 V.

The measurement of intermediate potentials is not straight forward, however. When considering overall reactions, potentials can be calculated from known energies of formation. Adsorbed intermediate species cannot be equated to a standard liquid or solid state. More importantly, the potential of any reaction depends upon the concentration of reactants and products; therefore the potential of the reaction

$$CO_2(g) + e^- \rightarrow \bullet CO_2^-(ad)$$

depends on [$\bullet CO_2^-$(ad)] as well as [CO_2(g)].

Despite these limitations, information on the potential of different intermediate reactions, if obtained at known intermediate concentrations will be useful as a route to allow the calculation of the relative concentration of alternative intermediate species. It is also interesting to consider the above in respect to the reactions promoted by Pd, this being the only electrocatalyst that has been associated with electrogenerative production of HCOOH, [3–5, 14]. This same electrocatalyst is the principal electrode that appears to form CO_2^-(ad) via the reaction [14].

$$M{-}H + CO_2 \rightarrow M{-}CO_2^-$$

and may also form CO_2^-(ad) with the aid of HCO_3^- and CO_3^- ions [4, 14, 48]. This means that Pd is the principal catalyst that does not require the formation of a $M{-}CO_2$ intermediate. If CO_2 reduction is the only significant cathode reaction, then calculations based on the free energy of formation indicate that formate formation would not be electrogenerative [3]. The existence of electrogenerative formate formation therefore confirms that other significant reactions must be occurring at a Pd cathode.

The pathway in which CO_2 is inserted into M—H bonds is also assumed to occur when CO_2 reduction occurs at 1.2 mA cm^{-2} at −0.4 V vs SCE on a polyaniline/Pt cathode, [49–51]. Unlike other cathodes discussed here the production of formate was accompanied by formaldehyde and ethanoic acid.

Schwarz et al. [52] have calculated potentials for a range of reactions forming reduced intermediate species from CO_2. Certain unverifiable assumptions have been made during these calculations, however. It should also be noted that the intermediate products referred to are in a solvated and not adsorbed state.

4. Electrocatalytic performance of different metals

Various workers have produced data concerning the end products obtained from systems catalysed by particular metals. Some have sought to extend this and develop a mechanistic approach allowing a more general overview of what product can be obtained from which type of metals under certain conditions. Hori et al. [37] give the findings shown in Table 2. Other findings do not agree with Table 2, although there is agreement about the uniqueness of Cu as an electrode.

Table 2. CO_2 reduction products reported by Hori et al. [37]

Metal	Reduction product
Cd, Sn, Pb, In	HCOOH plus CO
Zn	CO plus HCOOH
Ag, Au	CO
Ni, Fe	H_2 plus a small amount of CH_4
Ru	CH_3OH
Cu	H_2, C_2H_4, CH_4, HCOOH, CO depending upon conditions and surface preparation

Table 3. Electrodes operating with aqueous and nonaqueous electrolytes [33]

Metal	Outcome
Aqueous electrolyte	
In, Sn, Hg, Pb	Formate
Zn, Au, Ag	CO
Cu	Hydrocarbons, aldehydes alcohols
Al, Ga, Group VIII (except Pd)	Weak performance
Nonaqueous electrolyte	
Pb, Tl, Hg	Oxalate
Cu, Ag, Au, Sn, In, Zn	CO and CO_3^{2-}
Al, Ga, Group VIII (except those below)	CO and Oxalic
Ni, Pd Pt	CO only

Consideration of the merits of different electrocatalysts must include an awareness of the context in which data were generated. Early work used solid electrodes in liquid electrolyte. GDEs, introduced over the last few decades, are still being improved. Use of a proton exchange membrane in place of a liquid electrolyte has been tried over a number of years [53]. Early work was limited by the lack of active sites on the electrodes, with only low current densities being possible and the application of too high an overpotential leading to H_2 being the dominant product.

Table 3 shows a summary of work by Ikeda et al. [33], as reviewed by Jitaru et al. [7], which gave end products from electrodes operating with aqueous and non-aqueous electrolytes. Table 4 shows how several workers [48, 54] (reviewed by Jitaru [7]), took a more mechanistic approach. Jitaru et al. [7] conclude that there are four principal combinations, sp and d metal catalysts in aqueous or nonaqueous systems. The term 'sp metal' will also include any metal whose outer d orbital is usually full (e.g., Zn, Cd, Hg, Cu, Ag, Au) although these may not give a pure sp response, as well as those whose valence electrons are in the sp orbital.

Table 4. Electrodes catalysed by different group metals operating with aqueous and nonaqueous electrolytes [7]

Metal	Outcome	
	Aqueous electrolyte	Nonaqueous electrolyte
sp metals (Hg, In, Sn, Pb)	Formate	Oxalate (Tl, Pb, Hg)
sp metals (In, Sn, Cd, Zn, Cu, Ag, Au)		CO
d metals (e.g., Pt and Pd)	CO also HCOOH, HCHO, CH_3OH and hydrocarbons	CO (includes Ni)
d metals (e.g., Ru)	Hydrocarbons, alcohols, formaldehyde	
d metals (Fe, Cr, Mo, Ti, Nb)		Oxalate and CO

4.1. *sp metals in aqueous electrolyte*

A number of workers [26, 33, 48, 54–56] studying the sp metals Hg, In, Sn and Pb have generally found the characteristics of these metals to be similar, though some differences have been noted. Ito et al. [33] found Sn to have good overpotential characteristics (allowing high current densities) but low selectivity. In contrast to this Hara et al. [26] found Sn, Pb, Bi and In all to have very high selectivity. Differences found between these metals may reflect a failure to optimize the electrode manufacturing process, which will differ slightly for each metal. All the above metals favour the production of HCOOH and tend to suppress H_2 evolution. Udupa et al. [18] report that rotating Hg electrodes performed very well, and that sodium/mercury amalgam electrodes were operated at −1.7 V, making sodium formate, which migrates less than HCOOH. The process had the disadvantage of also producing sodium carbonate and bicarbonate, however, and it was necessary to maintain the correct pH and CO_2 levels.

Ito et al. [33] produced data showing the HCOOH selectivity of electrodes at different potentials against SCE. The results can be summarized as follows:

(i) In: selectivity fell to 83.2% as the voltage rose to −2.4 V, from a peak of 87.6% at −2 V.
(ii) Pb: selectivity fell to 78.9% as voltage rose to −2.4 V, from a peak of 80% at −2.3 V.
(iii) Zn: selectivity fell to 53.4% at −2.4 V, from a peak of 60% at −2.3 V, CO being the other main product.
(iv) Sn: selectivity fell to 37.6% at −2.4 V, from a 65% peak at −2.2 V, H_2 being the other product.

Mahmood et al. [45] also used Pb, In and Sn for developmental work on GDEs. They found that the results were generally good, but a high Tafel slope was exhibited which, for lead, increased with time, indicating the possibility of a barrier layer formed by a lead—CO_2 complex [57].

A study of the products obtained from Cu electrodes under different conditions supports the mechanisms proposed in Section 2; that is, conditions which promote ethanol formation also promote propanol and formaldehyde at the expense of CH_4. The critical step determining the composition is that of M—CO to M—C. [58]. Suppressing this step suppresses CH_4 production. Hara et al. [59] achieved this by a sulfide treatment of the cathode. GDEs made from Perovskite/copper oxide were found to give an increased yield of alcohols. Perovskite combinations with other metals were unsuccessful. Different electrolytes produced different results; some did not work. Reducing temperature increased CH_4 and C_2H_4 [13, 60, 61], Sullivan et al. [13] refer to a study using Cu electrodes showing that, as the applied voltage was increased, the maximum yield of different products occurred at different voltages HCOOH at −1.4 V, ethylene groups at −1.6 V and methane at −1.7 V. Further increases gave more H_2. Ohta et al. [62] found that the use of ultrasonics suppressed H_2 evolution; their peak voltage for CO_2 reduction was −1.9 V.

Cu does not follow the pattern for other sp metals. Jitaru et al. indicate that much work has been done with Cu, including cases where gas diffusion electrodes have replaced solid electrodes, giving a similar product profile but with current densities two orders of magnitude higher. Komatsu et al. [25] made a MEA using Nafion® 117 and Cu GDE. This gave C_2H_4 as the main product. Anionic membrane MEAs give HCOOH as the main product [3, 25].

The reactivity of Cu is partly explained by its readiness to form a Cu—CO^- species. This contrasts with Ag, for example, which does not form such a complex. The presence of Cu^+ ions or Cu complexing species in the electrolyte was also found to enhance performance [7].

Improved performances from sp metals were obtained by increasing pressure (up to 30 bar) [7]. This could be due to increasing the concentration of CO_2 at the electrode and also suppressing H_2 evolution. Mizuno et al. [19] described good results for In, Sn and Pb when operating at elevated pressure. Todoroki et al. [47] reported that In has produced HCOOH at 560 mA cm^{-2} using GDE in $KHCO_3$ solution at 60 atm pressure. Hara et al. [26] claimed HCOOH yields of over 90% on Sn, Pb and In at 30 bar, and a yield of over 50% on Cu and Bi. Ag and Au gave only a small yield of HCOOH at elevated pressures. Komatsu et al. [25] tried CO_2 at reduced pressures, that is, an atmospheric process with the reactant diluted by other gases. The HCOOH level rose significantly as the CO_2 partial pressure rose from 50% to 100%. If extrapolated this would suggest that elevated pressures would promote HCOOH formation over C_2H_4 for a Cu catalysed system. Kyriacou and Anagnostopoulos also showed HCOOH yield increasing more rapidly than any other reduction product as the CO_2 partial pressure rose towards 1 bar [30].

Jitaru et al. [7] noted that the performance of sp metals depended on the cation and anion present in the electrolyte and summarized work done by others [55, 56, 63]. Sp catalysed systems (e.g., In, Sn, Pb, or Bi) operating with a $KHCO_3$ electrolyte gave a high yield of HCOOH. Hg can also be included in this category, as a metal with the d orbital and both s orbitals filled. In contrast to this, systems catalysed by Zn or Cd gave some HCOOH but mainly gave H_2. The $d^{10}s^2$ structure of these two metals does not give the same performance as Hg. Systems catalysed by Ag or Au, which can be described as being an s^1 configuration, gave CO [7, 34]. Udupa et al. [18] obtained 20 mA cm^2 at −3.5 V giving 81.5% efficiency for the reduction of CO_2 to HCOOH using copper/mercury rods in sodium carbonate/sodium sulphate. Ikeda [64] found ZnO to be more electroactive than Zn, giving CO as the main reduction product.

Work done in quaternary ammonium salt (QAS) solution was also reviewed by Jitaru et al. [7]. Hg/graphite electrodes gave oxalate. Use of Pb promoted a further reduction reaction giving the glyoxalate. Use of pure Hg sent the reaction even further along the same reduction path giving malic acid [65]. The reaction giving the oxalate in QAS solution can be represented by

$$2{\bullet}CO_2^- \longrightarrow {}^-O_2C{-}CO_2^-$$

Use of graphite, Pb, Au, Ag, has given a range of products [7], the product profile being very dependent upon the applied potential.

It can be concluded [7] that the electrocatalytic activity (not necessarily the selectivity for formate nor the suppression of hydrogen evolution) takes the following order:

$$\begin{aligned} &In \approx Bi > Hg > Pb > Sn > Zn \\ &\quad \approx Cu > Cd > Ag > Au > Sb \end{aligned}$$

The main product from sp metals in aqueous electrolyte was formate, with H_2 and CO as the main alternatives. The s^1 metals gave predominantly CO and copper gave a range of products. The end product range obtained is compatible with the reaction pathways proposed in section 1, where the principal reactions were between CO_{2ad}^- and H^+ or H_2O_{ad} and the desorption of CO_2^-.

4.2. *sp metals in nonaqueous electrolyte*

In nonaqueous electrolyte, CO_2 solubility is higher and hydrogen evolution is suppressed. Most sp metals have been found either to give CO via disproportionation [34], oxalate or products down the oxalate pathway [16, 46]. Vassiliev et al. [46] gives the reaction pathway as being

$$({\bullet}CO_2^-)_{ad} + (CO_2)_{ad} \rightarrow (O_2C{-}{\bullet}CO_2^-)_{ad}$$

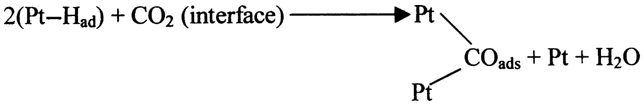
A yield of HCOOH was obtained while using a Pb cathode and a soluble Zn anode in TEAP/PrC [7]. A Pb cathode in a KOH/CH_3OH electrolyte gave HCOOH, CO, + CH_4 [66]. The solubility of CO_2 is high in methanol and, in such a system, Cu gave a good yield of CH_4 [7]. Ito and Ikeda [33] noted that a nonaqueous electrolyte behaves like an aqueous electrolyte following the addition of only a few percent H_2O.

4.3. *d group metals in aqueous systems*

Ni, Pd and Pt have all been shown to strongly adsorb CO_2. Extensive work has been done with platinum, and evidence has been found to suggest the existence of the species CO(ad), COOH(ad), HCOOH(ad) on cathode surfaces [7]. Studies have included how much reduction is occurring at the different planes of the platinum crystal [7, 67]. For Pt, CO is the dominant product evolved [7]. The principal reaction pathways for CO_2 reduction in aqueous media are those involving reactions between CO_{2ad}^- and H_{ad} or H^+. These give various 'reduced CO_2' species, which several workers have suggested could be linear CO(ad), bridged CO(ad), COOH(ad) and COH(ad) [7]. Additionally, Taguchi et al. [68] suggest that CO_2 reaching the interface of the adsorbed species on the electrode may displace adsorbed H as follows:

$$2(Pt{-}H_{ad}) + CO_2\ (interface) \longrightarrow PtCO_{ads} + Pt + H_2O$$

or



$$2(Pt{-}H_{ad}) + CO_2\ (interface) \longrightarrow Pt_2CO_{ads} + Pt + H_2O$$

Tomita et al. [69] confirmed the presence of $PtCO_{ads}$ and used a system that gave predominantly oxalate and formate.

Pd electrodes have also produced HCOOH, HCHO, CH_3OH and hydrocarbons [3, 7, 26, 34]. The presence of H(ad) was found to enhance yields of these [7]. In aqueous $KHCO_3$ solution, a Pd electrode gave HCOOH and CO and a Pd–Cu electrode gave the above plus methane and methanol. The Pd–Cu amalgam gave a greater efficiency, and this was thought to be due to the increase in adsorbed hydrogen. Sullivan et al. [13], however, describe Cu as having a very low H coverage, and the production of highly reduced products is consistent with an increased adsorption of reduced CO_2 species and a reduced H coverage.

Furuya [5] refers to a HCOOH producing cell, with one gas diffusion electrode with a Pd supported reactive layer and a second with a Pt supported layer. An ion exchange diaphragm separated them. CO_2 was supplied to the back of the Pd GDE and H_2 was supplied to the reverse of the Pt electrode. Aqueous carbonate and hydroxide solution were introduced into the spaces between the electrodes. This produced CO/HCOOH and was electrogenerative. Jitaru et al. [7] also refer to a similar cell. Furuya et al. [6] claimed an outstanding performance for a GDE with a Ru:Pd (1:1) cathode, where 80 mA cm^{-2} gave a 90% selectivity for HCOOH production.

Podlovchenko et al. [4, 14] claimed a HCOOH yield close to 100% under electrogenerative conditions. Use of a Pd wire in a 1 M $KHCO_3$ solution gave voltages up to 100 mV under equilibrium conditions. An applied voltage of 10 mV gave a reducing current density of 0.01 mA cm^{-2}. The Tafel slope was around 110 mV $(decade)^{-1}$. The proposed reaction was the substitution of CO_2 into the M—H bond. The presence of Cu reduced performance, presumably by reducing H_{ad}. Chaplin [3] obtained similar results. Ayers [17] describes an SPE system with a Pd catalysed cathode giving a yield (level not specified) of HCOOH at a partial current density of 0.1 A cm^{-2}.

Kudo et al. and Hara et al. [22, 26, 70] explored the benefits of increasing the cell pressure when using d-metal electrodes. Operation at 30 bar allowed a Pd electrode to produce significant levels of HCOOH even at very high applied potentials. Yields of CO and HCOOH were obtained from group 8–10 metals, Si and C, in contrast to the yield of H_2 obtained at 1 bar. Ito et al. [71, 72] reported that group VIII metals Fe, Co, Ni, Pd and Pt gave current efficiencies up to 62%, at pressures of 50–60 atm. A number of other references are given by Jitaru et al. [7], concluding that considerable benefits may be obtained by operating at elevated pressures. Hara et al. [26] used cyclic voltammetry to show CO_2 adsorption increasing at high pressures on all electrodes except group 4–7 metals and estimated that, for some systems, such increases would result in potential shifts of around 0.8 V. The mechanisms for improved CO_2 reduction could include increased levels of both H_{ad} and CO_2(ad).

Nickel has been used extensively [7]. The product range includes CO, hydrocarbons, and ethanol. Hydrogen evolution was also always present, although this could be minimized when the adsorbed CO covered the sites where H_2 would otherwise evolve. The adsorbed species Ni—CO was found by several workers [22, 23]. Kudo et al. [22] found that for Ni electrodes, the product profile changed with potential, giving more CO and HCOOH at more negative potentials and more hydrocarbons at less negative values. These workers proposed reactions, occurring in parallel, with relative rates depending on the potential:

$$CO_2 + e^- \rightarrow CO(ad) \qquad (\mathbf{A})$$

(presumably via CO_2(ad)). Reaction **A** competes with

$$H_2O + e^- \rightarrow H(ad) + OH^- \qquad (\mathbf{B})$$

The proposed reactions for CO(ad) were either the formation of CO gas at large applied potentials or hydrocarbons at lower potentials via the reaction

$$\begin{aligned} CO(ad) + 4H(ad) &\rightarrow {=}CH_2(ad) + H_2O \\ &\rightarrow \text{Hydrocarbons} \end{aligned} \qquad (\mathbf{C})$$

The selectivity for Reaction **C** diminishes as the applied potential increases.

HCOOH formation was proposed to occur via path **D**:

$$CO_2 + 2H(ad) \rightarrow HCOOH \qquad (\mathbf{D})$$

Reactions **A** and **B** compete. If **A** dominates then there is more CO and less hydrocarbons and HCOOH. Reactions **C** and **D** also compete. If **D** dominates then hydrocarbon production is suppressed. Large negative potentials promote **D** over **C**, which increases the yield of HCOOH, but may also promote **A** over **B**, which reduces the HCOOH yield. Thus, increasing the potential may either increase or decrease the selectivity for HCOOH, depending on the rival product. Other workers with Ni cathodes found evidence of linear and bridged CO(ad), with the linear disappearing at higher negative potentials [73]. Dimerization reactions have also been studied [74]. Jitaru et al. [7] and Hara et al. [26] also report other research with d metals in aqueous systems; this is summarized in Table 5.

4.4. *d Metals in nonaqueous electrolytes*

In this area Jitaru et al. [7] reported:

(i) Pt gave CO through disproportionation.
(ii) Pt in other experiments and also Ni gave mainly CO with lower levels of HCOOH.
(iii) Pd gave CO and oxalate. Fe gave oxalic/CO/H_2.
(iv) Others (e.g., Ti, Nb, Cr) gave mainly oxalic acid or further reduced products along that route. Mizuno et al. produced HCOOH and CO from H storing Ti cathodes used in a KOH/CH_3OH electrolyte [75].

Ru has interesting electrocatalytic properties, often performing in a manner similar to Cu. It has recently been used as the basis for novel electrocatalytic complexes [67] as have Cu and Co [76].

A wide range of nonaqueous electrolyte systems are available, and the exact product profile depends on the conditions used. Jitaru et al. [7] also include a discussion of mechanisms and equations, which give various products, and is mostly in agreement with the pathways shown in the previous sections.

5. Electron configuration of metals used as electrocatalysts, compared to final product profile

Many workers [7, 13, 16, 33], have explored the process variables affecting the final product profile produced by CO_2 reduction, and the principal variables have been found to be (i) the nature of the electrode, (ii) the nature of the electrolyte, (iii) the process temperature, (iv) the process pressure, and (v) the potential/current density of operation. Regarding the first of these, the macrophysical structure (i.e., solid electrode against GDE, or the nature of catalyst distribution within the electrode) will affect the number of active sites. For example, Yamamoto et al. recently reported the benefits of supporting electrocatalysts on activated carbon fibres [77].

The nature of the catalyst used will have the dominant effect on the final product profile. Given the importance of this, several researchers have explored options for classification of metals so that electrode performance can be expressed as some attribute (e.g., electronic structure) of the metal catalyst. Jitaru et al. [7] conclude that electrode performance can be primarily related to whether the metal has an sp or a d configuration and to whether the electrolyte is aqueous or nonaqueous. When reviewing available experimental data, it can be concluded that this is an oversimplification but a majority of the data do fit this pattern. A summary of the reactions promoted by these different groups of metals is

Table 5. Reactions of different metal electrodes

Metal	Electron configuration	Reactions/comments	Reference
Pb, Hg, Sn, In, Bi	s/sp	High HCOOH in aqueous medium, (some CO from Sn, In)	8, 45, 78
		Some rank In as best, others Pb	7, 33, 45,79
		Oxalate in nonaqueous medium for Pb, Hg	7, 20
		Glyoxalate to malic acid in QAS medium for Pb, Hg	7
		CO (disproportionation) for Sn, In nonaqueous + oxalate	33, 70, 80
		All gave very good yields of HCOOH in aqueous medium with high pressure.	26
Cu	$4s^1$/d group	A wide range reported, mainly CO, alcohols, hydrocarbons in aqueous.	13, 28, 31, 60 62, 81, 82
		CO in nonaqueous. HCOOH in high pressure (aq.)	7, 26, 76
		SPE membranes: Cationic gives C_2H_4. Anionic = HCOOH	3, 25
		CH_4 from a high pressure alcohol/ LiCl system	83
Ru	Part full d	Similar to Cu, (CO and CH_3OH, hydrocarbons) in aqueous	7, 29
(Os)		Also CH_4	13
Ni, Pd	Full d	CO in aqueous (all). Pd gave HCOOH,HCHO,CH_3OH +	7, 33
Pt		hydrocarbons	4, 14, 55
		HCOOH + CO in aqueous for Pt, Pd	26
		CO, hydrocarbons, ethanol for Ni in aqueous	22, 70
		CO in nonaqueous (all) also (low) oxalate and formate (all)	7, 33, 78
		Have been found to adsorb CO_2 very strongly	68
Fe, Co	Part filled d	Give bond to C atom for M–CO_2	13
Rh, W		Mainly H_2 in aqueous with increasing formate at high pressure	7
Ir, Re		(except W which gives H_2 at low pressure and everything but formate at high pressure), Co gave some CO at low pH, Re gave CO in CH_3OH.	26
		Fe gave oxalic/CO and H_2 in nonaqueous medium	84
Fe, Cr	Part full d	Oxalic and CO in nonaqueous (most give H_2 in aqueous, with	7, 33
Mo		carbon based yields increasing with pressure). Mo gave methanol via a reaction with the metal oxide.	26
Ti, Nb			
		Ti gave CO + HCOOH in a KOH/CH_3OH electrolyte	36
Zn	s only/s^1	CO (disproportionation) in aqueous (Zn, Ag, Au)	7, 13, 36, 85
Ag		CO also in nonaqueous (Zn, Ag, Au)	80, 86
Au,Cd		Some HCOOH at high pressure in aqueous (Ag)	26, 48
		HCOOH/H_2 in aqueous (Zn, Cd)	7
		CO, Oxylate and glyoxylate in nonaqueous (Zn, Cd)	
Groups 4 to 7	Less than half full d	H_2 in aqueous even at high P, no tendency to adsorb CO_2	26
Groups 7 to 10	Mostly full d	HCOOH only at high pressure in aqueous medium	26

shown in Table 5. Table 6 expands on this by showing aqueous and nonaqueous reaction products.

Ito and Ikeda [33] produced a table similar to Table 6, for performance in aprotic media. Metals in groups IV$_A$—VII$_A$ (with only partly filled d orbital) gave moderate yields of CO and oxalic acid. Metals from group VIII and B groups (mostly or completely filled d orbital) give a high CO yield but a very low oxalic acid yield. Pb, Tl and Hg give high oxalic acid and thus formed a third group. Ito and Ikeda proposed pathways similar to those previously discussed, namely:

Aqueous:

(i) reaction of CO_2^- with H^+ and e^- to give $HCOO^-$

(ii) removal of O group to give CO

Nonaqueous:

(i) dimerization of CO_2^- (ad) to give $(COO)_2^{2-}$ (plus further reductions)

(ii) disproportionation to give CO

6. Conclusion

It may be concluded that selection of an appropriate electrocatalyst and operating conditions is essential to the design of a selective CO_2 reduction process. The maximum reducing current is likely to be limited by the structure of the electrodes, including the distribution of electrocatalyst. The selection of the electrocatalyst should be done on the basis of the reactions that are inhibited as well as those that are promoted. For example, some metals with an sp electron configuration are suitable CO_2 reduction catalysts because of their tendency to inhibit H_2 evolution.

As soon as the reaction pathways have been established under one set of conditions, the effects of changing process conditions can be predicted, and the process can be optimized. Figure 5 shows the type of chart that can be used to assist this process. The chart

Table 6. Classification of metal electrodes

Metal	Configuration	Product in aqueous	Product in nonaqueous or aprotic
In Pb, Hg Sn, Bi	s/sp	High HCOOH (all) Small CO (disprop.) (Sn, In) Very high HCOOH at high, pressure (all)	High oxalate (all) Small CO (disprop.) (Sn, In) Glyoxylate, malate in QAS (Pb, Hg)
Zn, Ag Au, Cd	s/s^1	CO (disprop.) (Zn, Ag, Au) Also HCOOH/H_2 (Zn, Cd) Small formate at high pressure (Ag)	CO, oxylate, glyoxylate (Zn, Cd) CO (all)
Cu	s^1/d	Wide variety of products	CO HCOOH in SPE-anionic membrane
Ni, Pd Pt (bond strongly to CO_2)	Full d Group 10	CO (all) Various including HCOOH (Pd) HCOOH + CO (Pt, Pd) Various (not much HCOOH) (Ni)	CO (plus very low oxalate + formate)
Ru	Part full d (group 8)	Generally like Cu	CO (like Cu)
Fe, Co Rh, Ir	Part full d (group 8–9)	H_2 with some formate at high P M—CO_2 bond is to the C atom	CO + oxalate (small H_2)
Cr, Mo W, Ti Nb	Part full d (group 4–7)	H_2 only even at high pressure Very weak bonding to the CO_2	Oxalate + CO

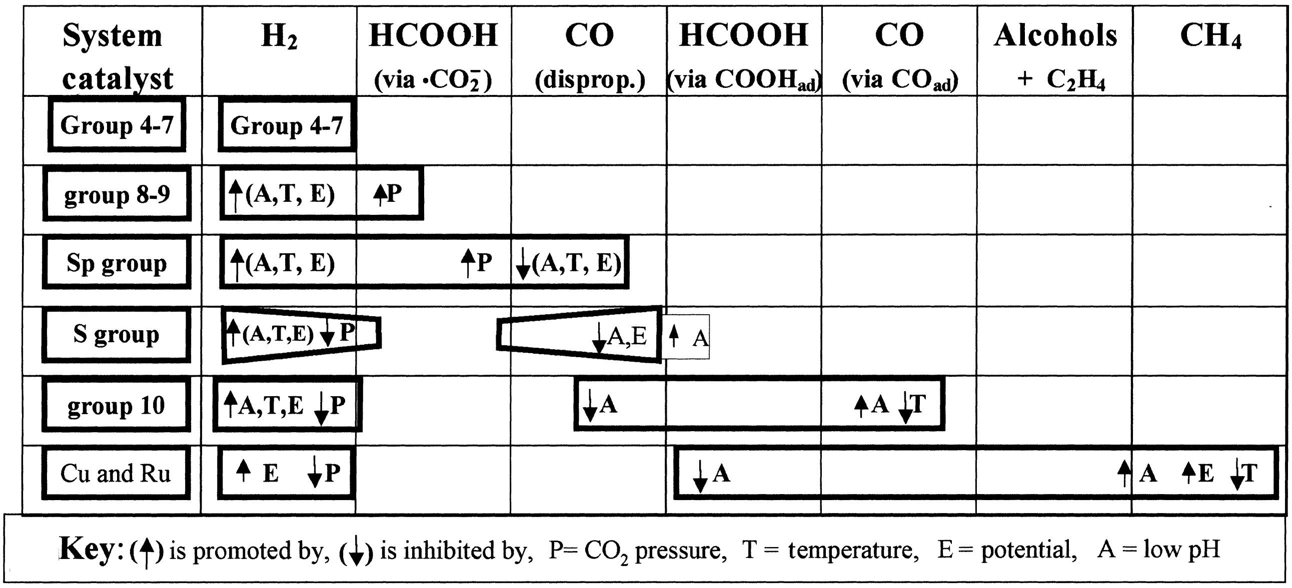


Fig. 5. Effects of process conditions on system performance.

shows an increasing tendency for the adsorption of CO_x^{y-} species in columns towards the right hand side. The indicators on the chart show that increasing temperature and applied potential will promote products on the left side, but high CO_2 pressure will block H_2 evolution. Low pH will block central products, that is, CO from disproportionation for s group catalysts and HCOOH for d group and Cu. It is expected that further work will be undertaken to develop an industrial process for the electroreduction of CO_2, following work recently funded by the EPSRC (UK) [87].

Figure 5 indicates the following main choices when selecting an electrode for formate production:

(i) *sp system such as In or Pb*. This is likely to have an optimum pH between 2 and 4, with low pH promoting H_2 evolution and high pH promoting CO production. Increased operating pressure will reduce H_2 evolution. Optimum operating temperatures are likely to be 50 to 100 °C. Increasing temperature will increase H_2 evolution but also improve CO_2 mass transfer; therefore the optimum temperature will depend upon the extent to which the process is limited by CO_2 mass transfer.

(ii) *d system such as Pd*. This appears to operate well in neutral pH electrolytes. Reduced pH will increase the yield of highly reduced products and eventually the H_2 yield also. Increased pH will increase CO yield. Increased temperature may reduce the yield of highly reduced products. It may be difficult to reduce CO yield by adjusting the process operating conditions.

(iii) *copper electrode*. This will follow a similar pattern to a d group system, but the optimum operating temperature and operating pH are both likely to be higher. The yield of CO will vary depending upon how the electrode is prepared. It may be possible to raise the operating temperature of a low H_2 yield system to above 100 °C.

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