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ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE MEDIATED BY MOLECULAR CATALYSTS

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CONTENTS

ABBREVIATIONS

bipy	2,2′-bipyridine
bpz	2,2′-bipyrazine
CB	conduction band
COD	cyclooctadiene
CV	cyclic voltammetry
diphos	1,2-bis(diphenylphosphino)ethane
DMF	dimethylformamide
dppene	*cis*-1,2-bis(diphenylphosphino)ethylene
FDH	formate dehydrogenase
GC	glassy carbon
MV^{2+}	1,1′-dimethyl-4,4′-dipyridinium
NHE	normal hydrogen electrode
PC	phthalocyanine

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PCTS	phthalocyanine tetrasulphonated
PEt_3	triethylphosphine
$P(OCH_3)_3$	trimethylphosphite
PPh_3	triphenylphosphine
SC	semiconductor
SCE	saturated calomel electrode
$TBuA^+$	tetrabutylammonium cation
TEOA	triethanolamine
terpy	2,2′:6,′2″-terpyridine
triphos	bis(2-diphenylphosphinoethyl)phenylphosphine
VB	valence band

A. INTRODUCTION

The transformation of CO_2 into organic substances is a promising long-term objective. It could allow the preparation of fuels or chemicals from a cheap and abundant carbon source. Among various possible approaches, the electrochemical reduction of CO_2 appears to be an attractive method. Indeed, studies on the electrochemical reduction of CO_2 on a metallic cathode were begun as early as the nineteenth century [1] and very early this century [2]. The main product was found to be formic acid. Early studies on CO_2 electroreduction in aqueous media are discussed in an excellent review [3] and in the references cited therein. Since this review will be concerned with several aspects of the electrochemical reduction of CO_2, it might be useful to have in mind the redox potentials of the various couples involving CO_2 and its reduction potentials. As shown by the $E^{\circ\prime}$ values given below [4], the nature of the reduction product has a strong influence on its thermodynamic accessibility from CO_2. Particularly important is the number of electrons involved in the reduction process: as expected, the redox potential becomes less and less negative as the reaction involves multielectronic pathways. In contrast, the value of the $CO_2/CO_2^{-\bullet}$ redox potential is -2.21 V(SCE) [4], making the monoelectron reduction mechanism highly unfavourable:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^{\circ\prime} = -0.52\ V \qquad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad E^{\circ\prime} = -0.61\ V \qquad (2)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E^{\circ\prime} = -0.48\ V \qquad (3)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^{\circ\prime} = -0.38\ V \qquad (4)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^{\circ\prime} = -0.24\ V \qquad (5)$$

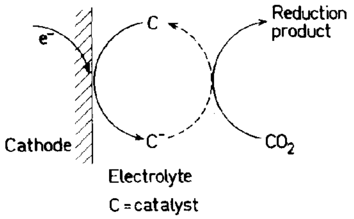
Many recent studies have also been devoted to the electroreduction of CO_2 on metal cathodes, either in aqueous or in low protic media. For instance, electroreduction of CO_2 on mercury was performed [5], leading mainly to oxalate ion if the solvent used (DMF) was sufficiently anhydrous. Other investigations have been carried out with various cathodic materials [6]. In particular, indium was claimed to be an interesting material allowing CO_2 electroreduction with a very low overvoltage [7]. Electroanalytical studies on tin and indium have recently been reported [8]. Unfortunately, indium does not seem to display the catalytic properties previously postulated, as shown by further investigations [9,10]. Use of rhodium [11] and ruthenium [12] cathodes gave low overpotentials, but with such materials whose catalytic properties for H_2O reduction to H_2 are excellent, the selectivity of CO_2 electroreduction in aqueous media is expected to be low. However, highly reduced products (CH_4 and CH_3OH) are found, making the ruthenium cathode a promising system.

The catalytic nature of the process using ruthenium cathodes [12] remains to be proven. Molybdenum has been shown to act as a useful cathodic material for generating methanol from CO_2, with low overvoltage [13], whereas CH_4 is formed on copper cathodes [14]. A particularly efficient system using gold electrodes has recently been described, leading to high faradaic efficiency for HCO_3^- reduction to CO, in aqueous media [15].

Semiconductors have also been used as cathodic materials, either in the dark [16–18] or under light irradiation. In the latter case, semiconductor suspensions have been used [19 23], or the reaction has been performed in a photoelectrochemical cell with a semiconductor cathode [24–29]. In general, the electrochemical reduction of CO_2 on metallic cathodes requires highly negative potentials (typically below -2 V(NHE)). In order to reduce energy consumption, the use of catalytic species in conjunction with the cathode is an appealing approach. Molecular electrocatalysts are promising in many respects because of the selectivity and efficiency associated with homogeneous catalysis. In addition, subtle variations in the structure of the molecular relay may be readily introduced by an appropriate synthetic procedure (organic skeleton) or by a fine control of the transition metal centre environment (ligands).

B. MOLECULAR ELECTROCATALYSTS IN SOLUTION

From an experimental viewpoint, the simplest way of associating an electrocatalyst, (whose function might be extremely complex but which very crudely might be regarded as a relay between the cathode and the reducible substrate) and a chemically inert cathode (that will only provide the system with electrons) is by dissolving the molecular electrocatalyst in the supporting electrolyte solution (or using it as such) of the electrochemical cell. This approach is evidently more straightforward than that of modifying the cathode surface by the electrocatalyst, as will be discussed in Section C. The



Scheme 1.

general principle of the system discussed in the present section is schematically represented in Scheme 1. The two most important families of electrocatalysts studied are macrocyclic complexes of first-row transition metals and platinum metal complexes of aromatic ligands such as bipy.

(i) Porphyrins and phthalocyanines

The first paper related to electrocatalytic reduction of CO_2 via nickel or cobalt PC was published in 1974 by Meshitsuka et al. [30]. Although strictly speaking this example does not belong to the system shown in Scheme 1, since the electrocatalyst is confined to the cathode–electrolyte interface, mention of this pioneering work should be made. The catalyst is deposited onto a graphite electrode by dip coating. The electrocatalytic phenomenon is clearly shown by comparing the *i–V* curves obtained under N_2 and under

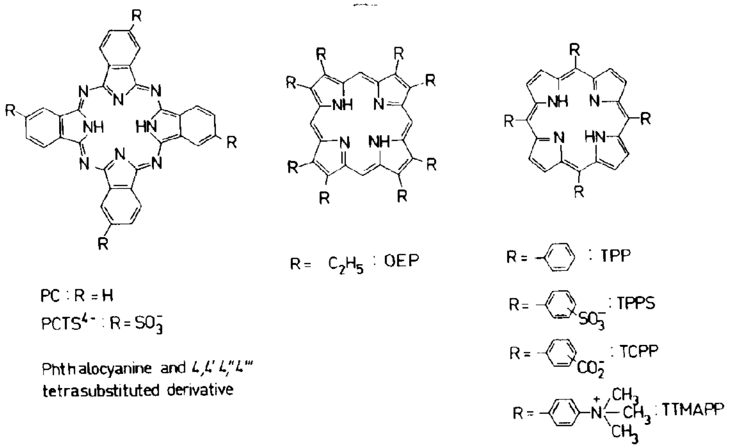


Fig. 1. Porphyrins and phthalocyanines used to prepare transition metal complex electrocatalysts.

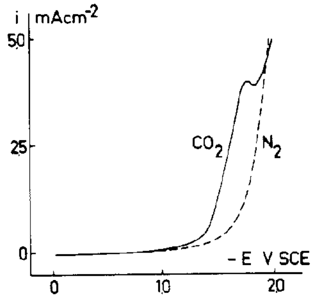


Fig. 2. Example of an $i-V$ curve.

CO_2 dissolved in an aqueous medium. An example of such $i-V$ curves is given in Fig. 2. If the supporting electrolyte is a quaternary ammonium salt, oxalic and glycolic acids are detected but no formic acid is found. Unfortunately, these early experiments were not followed by accurate and detailed analytical work concerning the nature and quantities of reduction products. However, this original system was slightly modified and re-examined ten years later by American researchers [31,32]. Their work will be discussed in Section C.

In 1977, other Japanese researchers were the first to use water-soluble tetrasulphonated phthalocyanine complexes (PCTS) of cobalt or nickel [33]. The same type of investigation was later extended to water-soluble porphyrins of cobalt, iron or copper [34]. Among the compounds examined, the cobalt porphyrin is the only one to display some catalytic activity. Although emphasis was put on electrochemical analytical methods ($i-V$ curves, capacitance-V curves), in the case of cobalt(II) *meso*-tetracarboxyphenylporphyrin, formic acid was detected using a colorimetric test.

More recently, palladium and silver porphyrins [35] (OEP) and (TPP) have been tested in CH_2Cl_2 (0.1 M TBA^+, BF_4^-). Ag^{II}(OEP), Pd^{II}(OEP) and Pd^{II}(TPP) show electrocatalytic activity, the major reduction product being oxalate. Unfortunately, long-time electrolysis is accompanied by partial decomposition of the catalyst, with formation of a silver mirror or palladium metal. Finally, in aqueous media and under CO_2 pressure (4–22 atm), the use of cobalt tetrakis(4-trimethylammoniophenyl)porphyrin iodide leads to CO formation ($\eta = 90\%$), with a small amount of HCOOH [36].

From the few publications discussed above, it is apparent that porphyrins and PCs of cobalt(II), nickel(II), silver(II) or palladium(II) in solution markedly decrease the overvoltage for reducing CO_2. Those catalysts lead to various reduction products, depending mainly on the metal and the solvent used. For instance, using silver(II) or palladium(II) porphyrins, oxalate is obtained in CH_2Cl_2 [35] whereas CO and HCOOH (besides H_2) are produced in aqueous media with other electrocatalysts [33,34,36].

(ii) Non-porphyrinic macrocyclic complexes of cobalt and nickel

Many of the tetraaza macrocyclic complexes synthesized in the past 20 years display structural analogies with metalloporphyrins [37]. In particular, square-planar geometries are highly favoured, with the possibility of coordinating additional ligands on the axial positions. However, the electronic properties of porphyrins are usually very different from those of other synthetic tetraaza macrocyclic ligands [38]. The overall charge borne by the ligand is −2 for porphyrins (and PCs) whereas many macrocyclic ligands are neutral. As a result, the redox properties of both classes of complexes are drastically different. In addition, the aromatic character of the porphyrin ligand might allow ligand-localized redox processes, the function of the central metal being much less important than for neutral ligands. Intuitively, it is easy to conceive that the charge localization within a reduced molecular electrocatalyst will have a drastic influence on its reactivity. If the electron density is more localized on the metal (*d* orbital for instance), the substrate

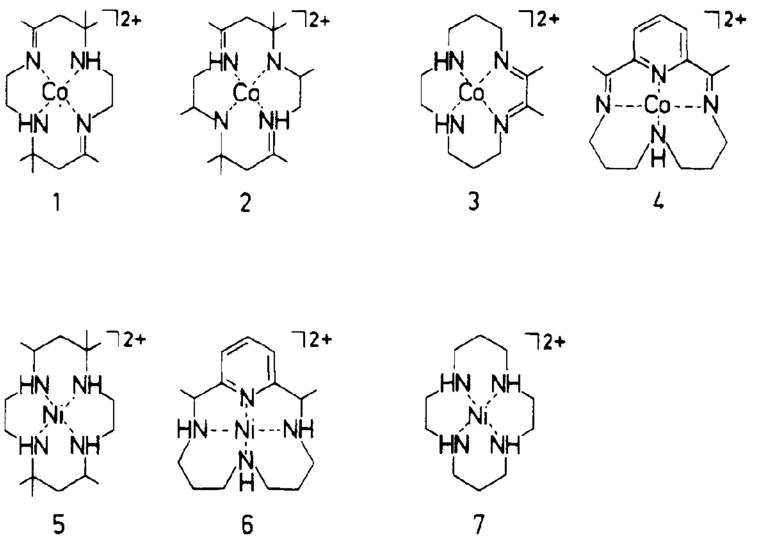


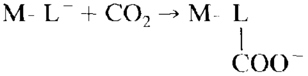
Fig. 3. Tetraaza macrocyclic complexes of nickel(II) and cobalt(II).

to be reduced will very likely interact directly with the metal. It might undergo oxidative addition or nucleophilic attack, leading to precursors of the reduction products. However, if the LUMO of the ligand is lower in energy than the vacant *d* orbitals of the metal, the charge will be localized on the ligand, which might change dramatically the course of the reaction. For instance, a reduced ligand could easily lead to irreversible carboxylation or protonation in the presence of CO_2 or H_2O respectively, making the corresponding coordination compound less likely to act as a catalyst.

The two different situations may be described by the following equations:

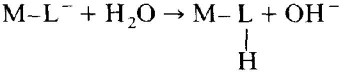
$$M{-}L \xrightarrow{e^-} [M{-}L]^- \tag{6}$$

where M = transition metal, and L = macrocyclic ligand (porphyrin type or other). The ligand-localized reduction is



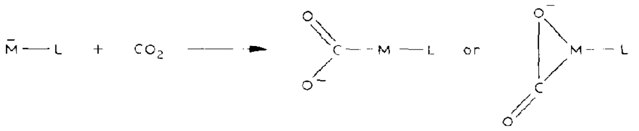
$$M{-}L^- + CO_2 \rightarrow M{-}\underset{\displaystyle COO^-}{\underset{|}{L}} \tag{7}$$

or

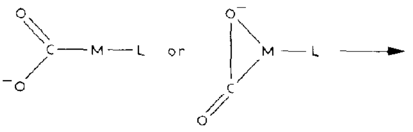


$$M{-}L^- + H_2O \rightarrow M{-}\underset{\displaystyle H}{\underset{|}{L}} + OH^- \tag{8}$$

The metal-localized reduction is



(9)



further reduction, protonation etc. leading to effective CO_2 reduction (10)

$$M\ {-}L + H_2O \rightarrow H{-}M{-}L + OH^- \tag{11}$$

$H{-}M{-}L \rightarrow$ further reduction, protonation,
insertion etc. leading to H_2
production or CO_2 hydrogenation (12)

TABLE 1

Complex	Solvent (v/v)	Potential	η_{CO}	η_{H_2}	η_{CO+H_2}	Turnover number	Ref.
1	CH_3CN-H_2O (1/2)	−1.6	50	50	93	7.8	39
	CH_3CN-H_2O (1/2)	−1.5	50	50	90	9	39
2	CH_3CN-H_2O (95/5)	−1.55	36.3	19.7		3	43
	DMF-H_2O (95/5)	−1.6	56.2	25.0			
3	DMF-H_2O (95/5)	−1.6	13.3	58.8	1	4	43
4	DMF-H_2O (95/5)	−1.3	66.4	5.3	71	7	43
5	CH_3CN-H_2O (1/2)	−1.6	66	33	98	6	39
6	CH_3CN-H_2O (1/2)	−1.3	–	–	44	2.1	39
7	H_2O	−1.3	96	0	96	32	48

The somewhat simplistic image described above only accounts for the general behaviour of first-row transition metal complexes containing macrocyclic ligands (porphyrinic type and others). Second- and third-row complexes containing bipy-type ligands will be discussed in Section B(iii).

The first investigation using non-porphyrinic-type macrocyclic complexes was reported by Fisher and Eisenberg in 1980 [39]. This paper was a real landmark in the field of CO_2 electroreduction, not only because of the compounds used but also for the quantitative analysis of the reduction products that it contains. In particular, the two major products are gaseous: CO and H_2. Some of the most representative results obtained with macrocyclic complexes of nickel(II) or cobalt(II) are collected in Table 1. In H_2O or H_2O-CH_3CN and on a mercury pool, reduction of CO_2 occurs at potentials in the range −1.3 to −1.6 V(SCE). CO and H_2 are obtained in the same ratio for almost all experiments (CO : H_2 ratio 2 : 1). From Fisher and Eisenberg's study, several points are particularly noteworthy.

(1) The electrocatalytic nature of the process is certain: blank experiments performed without CO_2 or catalyst lead to no CO formation.

(2) The reaction is catalytic in the sense that the nickel or cobalt complex undergoes several catalytic cycles (the turnover number, equal to moles CO produced/moles of electrocatalyst introduced, can be almost ten).

(3) The complexes used are stable over a period of 24 h and there is no evidence for their decomposition at the end of an electrolysis.

(4) Protons are necessary; in the absence of any proton source, the cobalt or nickel complexes are reduced to the monovalent state but there is no further reaction with CO_2.

(5) From the reduced complexes, two competitive pathways may be operating: reduction of H^+ to H_2 or reduction of CO_2 to CO. The latter process might involve the reaction between CO_2 and a hydride formed preliminarily (Co–H or Ni–H).

The supporting electrolyte is in some cases KNO_3 (0.1 M). For these experiments, it might be that partly erroneous results were obtained, owing to parallel electroreduction of nitrate ions. Indeed, it was recently shown that NO_3^- electrochemical reduction is efficiently catalysed by some macrocyclic complexes of nickel [40–42] or cobalt [40,41].

The work of Tinnemans et al. [43] in H_2O–CH_3CN or H_2O–DMF with complexes **2**, **3** and **4** of Table 1 confirm the results of Fisher and Eisenberg. The CO-to-H_2 ratio strongly depends upon the experimental conditions used (applied potential, percentage of water in the solvent etc.). The overall amount of gas produced (CO + H_2) decreases if the water concentration decreases. The selective reduction of CO_2 compared with water is favoured at accessible and not very negative potentials (-1.15 to -1.45 V(SCE)).

One of the most popular macrocyclic ligands used for decades in coordination chemistry is 1,4,8,11-tetraazatetradecane, universally known as cyclam [44]. With a large variety of transition metals, it leads to highly stable and kinetically inert complexes [45]. Some of the cyclam complexes are also known to display catalytic properties in several reactions (O_2 reduction [46], nitrate reduction [40], olefin epoxidation [47] etc.). Ni(cyclam)$^{2+}$ has been used as an electrocatalyst for CO_2 reduction in a purely aqueous medium [48,49]. It displayed exceptional properties, the selectivity of the process (CO-to-H_2 ratio in the gas produced) being surprisingly high in the presence of Ni(cyclam)$^{2+}$. Some typical i–V curves for the nickel(II) reduction under CO_2 or argon are presented in Fig. 4.

Some of the most characteristic properties of the system are the following.

(1) High turnover frequencies (up to 10^3 cycles h^{-1}) could be obtained.

(2) Accessibility of the applied potential: the electrocatalytic process starts at -0.9 V(NHE).

(3) At pH 4.1, only CO is formed as a reduction product with a faradaic yield of 99%.

(4) The catalyst is particularly chemically resistant, the efficiency of the reductive process remaining constant over long electrolysis periods and after large overall turnover numbers (the ratio of the CO produced to the Ni(cyclam)$^{2+}$ present is greater than 10^4).

The presence of carbonylated complexes of nickel(I) during the reaction was clearly demonstrated by spectroscopic methods (UV–visible, IR, EPR),

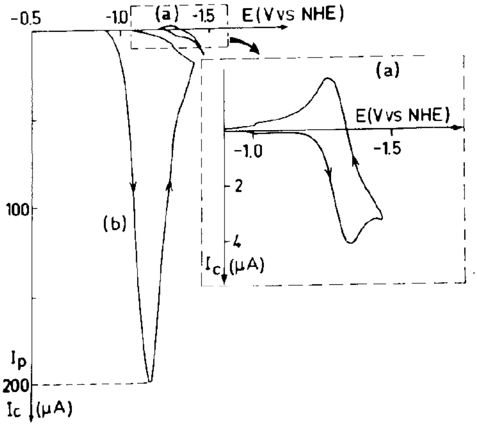
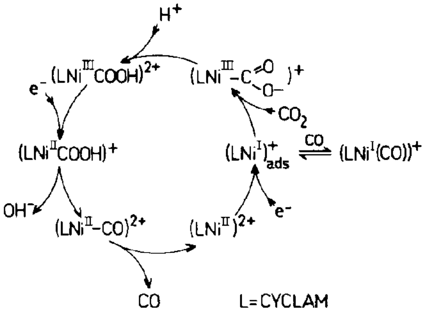


Fig. 4. Typical *i*–*V* curves for the Ni(cyclam)$^{2+}$ reduction under CO_2 or argon.

either in aqueous media or in DMF. These compounds correspond to the three-electron reduction products of Ni(cyclam)$^{2+}$ and CO_2:

$$Ni^{II}(cyclam)^{2+} + CO_2 + 3e^- + 2H^+ \rightarrow Ni^{I}(CO)cyclam^+ + H_2O$$

The characterization of Ni(CO)cyclam$^+$ in the medium does not prove its involvement in the catalytic cycle, but this compound can easily liberate CO in water with regeneration of an active unsaturated nickel species. The instability of the carbonyl complex of nickel(I) in water compared with organic solvents may explain the greater efficiency of the catalytic system in aqueous media or in comparison with DMF. A possible reaction scheme of the general type ECEC is presented in Scheme 2. In addition to the criteria of thermodynamic and kinetic stability which are attached to the unique



Scheme 2.

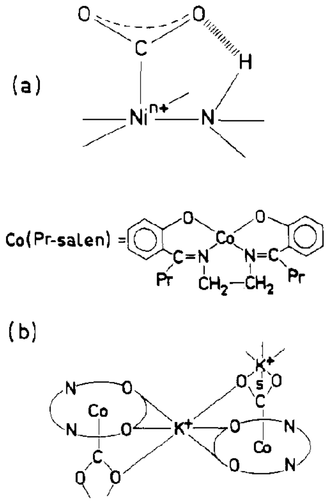


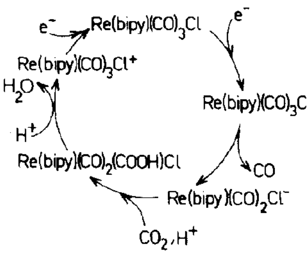
Fig. 5. Intermediate species in the selective reduction or binding of CO_2.

properties of Ni(cyclam)$^{2+}$ compared with related but different macrocyclic complexes, other factors have to be taken into account. In particular, species adsorbed onto the electrode surface play an important role in the reduction mechanism. Furthermore, this phenomenon might be, in part, responsible for the surprisingly high shift (300 mV) in the reduction potentials of the nickel(II) complexes under either argon or CO_2.

Geometrical factors could also determine the selective properties of Ni(cyclam)$^{2+}$. Intermediate species as represented in Fig. 5 might also explain why CO_2 is so selectively reduced (and initially, bound to the nickel centre) in the presence of water as solvent. It may be speculated that hydrogen bonds are formed between an oxygen atom of CO_2 and the hydrogen atom of a secondary NH amine group of the cycle, by analogy to what has previously been observed in the reaction of cobalt(I) complexes with CO_2 [50]. In this case, the edifice is stabilized by an additional interaction between an oxygen atom of the CO_2 molecule bound to cobalt and a potassium cation serving as a Lewis acid [50] (see Fig. 5).

(iii) Transition metal complexes of 2,2′-bipyridine and related ligands

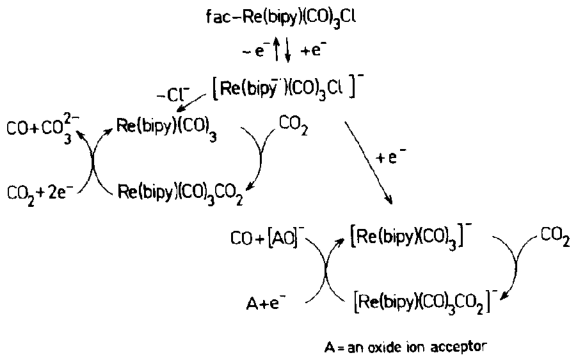
Several groups have explored the possible use of nickel [51], cobalt [52], rhenium [53,54], ruthenium [55,56], rhodium, iridium and osmium complexes [57] of bipy-type ligands in the electroreduction of CO_2.



Scheme 3.

Hawecker et al. had previously shown that Re(bipy)(CO)$_3$Cl can be used in photochemical systems of CO_2 reduction for generating CO in the presence of an organic electron donor [53]. Subsequently, it was clearly established that this same complex leads to selective electroreduction of CO_2 to CO at −1.5 V(SCE) in DMF–water (9 : 1 v/v). Under given conditions, high faradaic yields (98%) and large overall turnover numbers for rhenium (several hundreds) could be obtained, without significant damage of the system or loss of activity. Strict control over the experimental conditions seems to be of crucial importance with respect to the efficiency and selectivity of the system. In particular, the presence of coordinating anions such as Cl is highly favourable, since it prevents the formation of an inactive rhenium(0) dimer, [*fac*-Re(bipy)(CO)$_3$]$_2$ which has been isolated and characterized. For the process to work, it is essential that a vacant site on the metal in Re(bipy)(CO)$_3$Cl be protected by an excess of coordinating anion in order to inhibit the dimerization reaction and subsequent reduction of protons to H_2. The proposed catalytic cycle is represented in Scheme 3.

Using the same complex as that used by Lehn and his group, Re(bipy)(CO)$_3$Cl, Meyer and coworkers have studied in detail the mechanism of the CO_2 reduction in an aprotic medium (CH_3CN) [54]. Complexes of the type Re(bipy)(CO)$_3$X where X = H–, HCOO– or HOCOO– were isolated and characterized. In particular, it was shown that Re(bipy)(CO)$_3$H undergoes a photo-insertion reaction with CO_2 to give the formate complex Re(bipy)(CO)$_3$(HCOO). Without light irradiation of the hydrido complex, the same insertion reaction occurs but at a noticeably slower rate. Electrolysis at a fixed potential (E = −1.55 V(SCE)) of a saturated solution of CO_2 in CH_3CN and in the presence of Re(bipy)(CO)$_3$Cl produces no formate but only CO and CO_3^{2-}. The authors suggested that two mechanisms of CO_2 reduction occur simultaneously, the common intermediate being the unsaturated species Re(bipy)(CO)$_3^-$. The two proposed pathways of CO_2 reduction are indicated in Scheme 4.



Scheme 4.

Apart from the rhenium system, the most used and studied complexes in the electrocatalysis of CO_2 reduction are those of ruthenium(II) [55,56], namely $Ru(bipy)_2(CO)_2^{2+}$ and $Ru(bipy)_2(CO)(Cl)^+$. Electrolysis performed in CO_2 saturated aqueous DMF (10 vol.% H_2O) at a potential of -1.3 to -1.5 V(SCE) and in the presence of $Ru(bipy)_2(CO)_2^{2+}$ leads to variable amounts of CO, $HCOO^-$ and H_2. Various experimental factors have been studied: potential, (water content), pH and pK_a of the acid used as a proton source. It was postulated that an unstable ruthenium(0) complex was formed by dielectronic reduction of $Ru(bipy)_2(CO)_2^{2+}$. This pentacoordinated species, $Ru(bipy)_2(CO)$, would then react with CO_2 and lead to a formate complex, the precursor of either CO or $HCOO^-$ formation, depending on the pH.

Finally, other rhodium, ruthenium and iridium complexes have been proposed as electrocatalysts of CO_2 reduction to CO or $HCOO^-$, in anhydrous CH_3CN and with $TBuA^+PF_6^-$ as supporting electrolyte [57]. CV experiments performed under CO_2 show current intensity increases in the potential range -1.2 V to -1.7 V(SCE). The following complexes have been tested: $Rh(bipy)(COD)^+$, *cis*-$Rh(bipy)_2(CF_3SO_3)_2^+$, *cis*-$Ir(bipy)_2(CF_3SO_3)_2^+$, $Ru(\eta^6\text{-}C_6H_6)(bipy)Cl^+$, $Ru(terpy)(dppene)Cl^+$.

Fine product analysis after electrolysis of CO_2 in the presence of *cis*-$Rh(bipy)_2(CF_3SO_3)_2^+$ revealed tri-*n*-butylamine and 1-butene in addition to $HCOO^-$ and H_2. This is a clear indication that the supporting electrolyte is partially consumed during the course of the reaction.

(iv) Phosphine complexes

It is paradoxical to see that the numerous phosphine complexes known and extensively used in homogeneous catalysis (hydrogenation, hydroformylation and hydrosilylation of olefins, for instance) have been so little used as electrocatalysts for CO_2 reduction. Interestingly, the vast majority of isolated and crystallographically characterized CO_2 complexes of various transition metals [58–62] contain phosphines or arsines as ancillary ligands.

$Rh(diphos)_2Cl$ has been used in anhydrous CH_3CN [63]. At -1.55 V vs. Ag wire, $HCOO^-$ is obtained with a faradaic yield of 22–42%, depending on the electrolysis time. It is suspected that CH_3CN is the proton source necessary for the formation of $HCOO^-$, small amounts of $CN–CH_2–COO^-$ being detected.

Palladium complexes of the type $[Pd(triphos)L][BF_4]$ with $L = CH_3CN$, PEt_3, PPh_3 or $P(OCH_3)_3$ have been prepared and tested in acidified CH_3CN [64]. The palladium complexes showed some catalytic activity, whereas their isoelectronic and isostructural nickel and platinum analogues were completely inefficient. For the palladium complexes, electrolyses under CO_2 and with 10^{-2} M HBF_4 produced CO and H_2 (with a CO-to-H_2 selectivity of up to three) but the turnover numbers obtained on palladium remain low (ten or below). Although the electrocatalytic nature of the process was clearly evident, the catalytic complexes were only active for short periods of electrolysis (30 min).

(v) Polymetallic complexes and other electrocatalytic systems

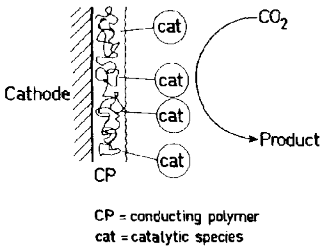
In this section we shall describe two novel systems which were recently reported: an iron–sulphur cluster $[Fe_4S_4(SR)_4]^{2-}$ ($R = -CH_2–C_6H_5$) and a system based on Everitt's salt.

In 1982 it was reported [65] that CO_2 is electroreduced at about -2 V(SCE) in DMF in the presence of $[Fe_4S_4(SR)_4]^{2-}$. The formation of $HCOO^-$ was shown to be favoured compared with that of oxalate or CO by the presence of the tetranuclear cluster. Owing to the very negative potential applied, it was postulated that the proton required in the reaction is provided by the tetraalkylammonium salt used as the supporting electrolyte. More recently, the same group extended its investigations to other 4Fe–4S clusters by replacing the benzylthiolate initially used by t-BuS$^-$ and PhS$^-$ [66]. In addition, mixed clusters (Mo–Fe–S or W–Fe–S) were also tested. Unfortunately, under the electrolysis conditions used (-2.0 V(SCE)) the cluster structures are rapidly destroyed.

Intriguing results were recently reported on the electroreduction of CO_2 to methanol [67–69]. Although mechanistic considerations are only highly speculative at the present stage, it seems that a polynuclear mixed-valence iron complex (Everitt's salt) is involved in the reaction. Other related polymeric inorganic materials also display electrocatalytic properties. The main problem in this system is that methanol is required as a cosolvent, making the titration of the CH$_3$OH produced particularly difficult and inaccurate.

C. USE OF CATHODIC MATERIALS MODIFIED BY SURFACE DEPOSITION OF MOLECULAR ELECTROCATALYSTS

The electrocatalytic systems discussed below are based on the general principle given in Scheme 5. Although the work of Wrighton and coworkers [70] does not strictly belong to the family of systems discussed in this section, it is worth mentioning here briefly. When particles of palladium metal are embedded in a polymer matrix containing an appropriate electron relay (methyl viologen or analogue), the composite material obtained after deposition (or anchoring) onto a cathode surface can act as an electrocatalyst. In particular, CO$_2$ is electroreduced selectively to formate, in agreement with previous studies of Klibanov et al. [71] on the particularly interesting catalytic properties of palladium with respect to CO$_2$ reduction to formate. Wrighton and coworkers have used a cathodic material consisting of a metal support (tungsten or platinum) covered with a redox polymer prepared from V^{2+} (see Fig. 6) and impregnated with palladium particles generated in situ by reduction of PdCl$_4^{2-}$, the counter-ion of V^{2+}. At very accessible potentials (-0.8 V(SCE)), relatively good faradaic yields of formate ($\eta = 50$–85%) were obtained in aqueous CO$_3$H$^-$ (0.1 M). The efficiency of the electrode decreases with time but it was demonstrated that the electroreductive process is indeed electrocatalytic in nature with respect to palladium and the electron relay (poly-V^{2+}).



Scheme 5.

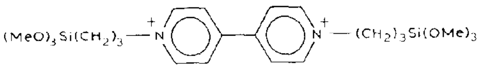


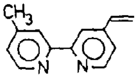
Fig. 6. Precursor (V^{2+}) of the redox polymer.

Following the pioneering work of Meshitsuka et al. [30] and Hiratsuka et al. [33], on the electrocatalytic properties of NiPC and CoPC, as discussed above, two other groups have deposited transition metal phthalocyanines onto glassy carbon by dip coating and used the corresponding materials as cathodes for electroreducing CO_2.

The recent study of Kapusta and Hackerman [31] shows that using CoPC as electrocatalyst, $HCOO^-$ is the main reduction product at $pH > 5$ ($\eta = 60\%$) in an aqueous electrolyte. At more acidic pH, methanol is also formed in small quantities ($\eta = 5\%$ at pH 3). For the other metallophthalocyanines tested, the activity sequence is $CoPC > NiPC \gg FePC, CuPC > CrPC^+$.

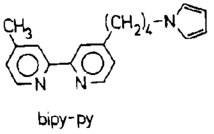
Under experimental conditions very similar to those used by Kapusta and Hackerman, other authors [32] obtained mainly CO and H_2 in a ratio of 1.5 : 1 (pH = 5; 1 atm CO_2; applied potential, −1.15 V(SCE)). The turnover number of CoPC is very large (greater than 10^5). It is not clear which experimental factors are responsible for the dramatic difference between the products formed in the two studies discussed above. Perhaps the main point is that, notwithstanding the reduction products obtained, decomposition of the electrocatalyst in the bulk of the solution can efficiently be inhibited by immobilizing the metallophthalocyanine at the electrode surface.

In recent years, several groups have taken advantage of the electrocatalytic properties of $Re(bipy)(CO)_3Cl$, as previously shown by Lehn and coworkers [53], to build modified electrodes in view of electroreducing CO_2. The rhenium complex could be derivatized and incorporated into a polymeric film formed at the interface between the electrolyte and the electrode (metal or semiconductor). The groups of Meyer [72] and Abruna [73] used a vinylic derivative as a monomer precursor, $Re(vbipy)(CO)_3Cl$ where vbipy is 4-vinyl-4′-methyl-2,2′-bipyridine:



vbipy

CV experiments provided clear evidence that a polymeric film is indeed formed which displays the characteristic properties of $Re(bipy)(CO)_3Cl$ [72]. Using such a modified platinum electrode in CH_3CN, CO_2 is electroreduced (−1.55 V(SCE)). Unfortunately, after a few hundred turnover numbers, the electrocatalytic activity of the modified electrode is completely lost. In order to deposit the rhenium electrocatalyst onto a cathode surface, Deronzier and coworkers [74] have used another approach based on functionalized polypyrrole. They used 4[4″-(*N*-pyrrolyl)-*n*-butyl]-4′-methyl-2,2′-bipyridine (bipy–Py) as ligand:



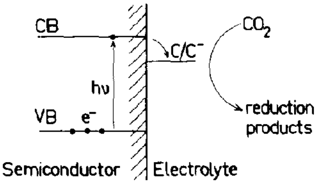
The complex Re(bipy-Py)$(CO)_3Cl$ could be electropolymerized on platinum by oxidation at +0.95 V (vs. Ag/Ag^+), analogously to several *N*-substituted pyrroles bearing electroactive pendent groups [75–77]. In a typical experiment, the electroactive film (containing 9.4×10^{-7} mol rhenium complex) leads to the formation of 5.0 ml CO after 170 min electrolysis ($E = -1.85$ V) in CO_2-saturated anhydrous CH_3CN with a faradaic yield of 78%. Here again, the electroactivity of the material strongly decreases within a few hours. Small amounts of oxalate are also found, the mechanism of its formation being still unclear.

Although it is difficult to compare the systems based on film modified electrodes [72,74] with that containing the rhenium complex in solution [53], it is not obvious that the electrocatalyst is more resistant when used as a polymeric deposit than when dissolved in the electrolyte. Finally, it is worth mentioning an additional modified electrode system employing an electropolymerized nickel(II) tetraazaannulene complex (on GC or platinum) [78]. The formation of formate was clearly evident from labelling experiments using $^{13}CO_2$ as substrate.

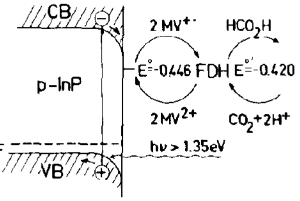
D. PHOTOELECTROREDUCTION OF CO_2 ON SEMICONDUCTORS, CATALYSED BY MOLECULAR SPECIES

Such systems are especially appealing since an important energy input contribution from light might be expected, thus diminishing electricity consumption. The general principle of the strategy followed is described in Scheme 6.

Many researches have been devoted to the direct photoreduction of CO_2 at the surface of semiconducting materials (powders in suspension or photoelectrodes) without the assistance of any catalytic molecular species. For



Scheme 6.



Scheme 7.

instance, p-Si [26,79], p-CdTe [80], p-InP [29], pGaP [19,82], n-GaAs [18,81] and other materials have been used. The use of semiconductors in conjunction with molecular or enzymatic catalysts has recently been proposed by several research groups.

In 1982, a brief report was made by Bradley and Tysak [83] on the photoelectroreduction of macrocyclic nickel and cobalt complexes in CH_3CN, on irradiated ($\lambda = 633$ nm) p-Si at a redox potential of -0.9 V(SCE). This publication was rapidly followed by another short report [84] on the possible use of the system for photoelectroreducing CO_2 to CO in CH_3CN–H_2O (1/1 v/v) on p-Si. In this case, good faradaic yields of the H_2 and CO mixture (2 : 1) were obtained. Beley et al. [85] have reported a photoelectrochemical system based on p-GaAs in conjunction with $Ni(cyclam)^{2+}$ in aqueous media. CO and H_2 are the reduction products, the applied potential being ca. -0.95 V(NHE). More interesting is the analogous system using p-GaP as the semiconducting photocathode [86]. In this particular case, the selectivity could be greatly improved (CO-to-H_2 ratio, up to 50) and the applied potential could be made much more accessible (-0.2 V(NHE)). A special photoelectrochemical cell was described in 1983 by Parkinson and Weaver [87]. It takes advantage of an enzyme, (formate dehydrogenase (FDH)) which is able to catalyse CO_2 reduction to $HCOO^-$ in the presence of a reducing species such as $MV^{+\cdot}$. The latter is photoelectrogenerated from MV^{2+} on p-InP. The overall reaction scheme is indicated in Scheme 7. The faradaic yield is in the range 80–93%. Problems attached to the denaturation of the FDH enzyme by O_2 and stirring are still limiting factors.

E. PHOTOCHEMICAL REDUCTION OF CO_2 IN HOMOGENEOUS AND MICRO-HETEROGENEOUS SYSTEMS

In the catalytic reduction of CO_2 by a molecular species, the initial step is the reduction of the molecular catalyst prior to electron transfer to CO_2. Until now, we have examined the cases for which the electron source is a cathode (metal, glassy carbon, semiconductor), the electron being either transferred at the interface between the electrode and the molecular catalyst in solution or being injected into a surface film containing the electrocatalyst. Another approach is to provide the electrons for the system via an intermediate photochemically generated reductant. The reducing species can be obtained either by direct absorption of light leading to a strongly reducing excited state or by quenching of the excited state of a photoactive species by an electron donor, followed by formation of the reduced state of the catalyst. Owing to its exceptional photoredox properties, the complex $Ru(bipy)_3^{2+}$ has been widely employed in a large variety of systems related to light energy conversion to chemical [88,89] or electrochemical [90] energy. It has also been used for photochemically reducing CO_2 to CO [91] or formate [92,93]. When $Ru(bipy)_3^{2+}$ is associated with a complex of cobalt(II) or $Ni(cyclam)^{2+}$ and an irreversibly consumed electron donor (tertiary amine) or ascorbic acid, CO_2 is converted to CO and H_2 under visible light irradiation [52,94,95]. In this case, the general mechanism seems to be well established. It corresponds to the following series of reactions:

$$Ru(bipy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bipy)_3^{2+}$$

$${}^*Ru(bipy)_3^{2+} + D \rightarrow Ru(bipy)_3^{+} + D^{+\cdot}$$

(D, electron donor)

$$D^{+\cdot} \rightarrow D_{ox} \text{ (oxidation products)}$$

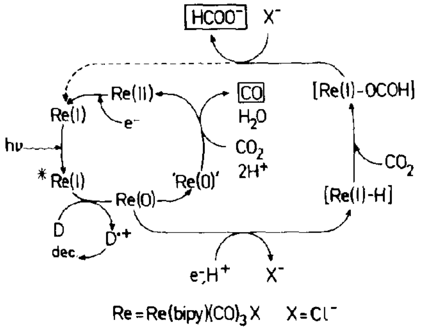
$$Ru(bipy)_3^{+} + Co^{II} \text{ complex} \rightarrow Ru(bipy)_3^{2+} + Co^{I} \text{ complex}$$

$$Co^{I} \text{ complex} + 1/2CO_2 + H^+ \rightarrow Co^{II} \text{ complex} + 1/2CO + 1/2H_2O$$

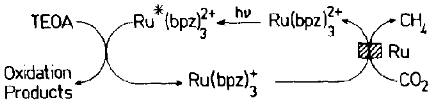
and

$$Co^{I} \text{ complex} + H^+ \rightarrow Co^{II} \text{ complex} + 1/2H_2$$

The CO-to-H_2 ratio in the gas produced in highly dependent on the experimental conditions used and on the nature of the starting cobalt(II) complex. Other photochemical systems based on ruthenium complexes have recently been described. Irradiation of $Ru(bipy)_3^{2+}$ in DMF–TEOA in the presence of CO_2 leads preferentially to formate formation [92,93]. It is very likely that some photochemical dissociation of $Ru(bipy)_3^{2+}$ to $Ru(bipy)_2L_2^{n+}$ ($L = H_2O$, DMF) takes place, the bis(bipy) complex being the active species in the CO_2 reduction process [92]. The complex $Re(bipy)(CO)_3Cl$, already mentioned for its electrocatalytic properties, was first utilized in a remarkable photochemical system [53]. Irradiation of this compound in its metal-to-ligand charge transfer band (ca. 400 nm) leads to CO_2 reduction to CO while an organic electron donor is oxidized. In the presence of Cl^-, high quantum yields (up to 14%) have been obtained [94]. Without coordinating



Scheme 8.



Scheme 9.

anions such as Cl^-, it has been possible to isolate a formato rhenium complex. The main feature of the rhenium complex is that it acts simultaneously as a photoactive species and as a precursor of the catalytic centre. The mechanism proposed by the authors [94] is in agreement with other detailed studies [54,96–98]. It is given in Scheme 8.

Finally, a recent report describes a photochemical system of CO_2 reduction to methane [99]. The photoactive complex is $Ru(bpz)_3^{2+}$ which undergoes reductive quenching of its metal-to-ligand charge transfer excited state by an organic electron donor. The formally monovalent ruthenium complex thus obtained reacts with CO_2 in the presence of a colloidal ruthenium metal catalyst to produce CH_4. Another slightly modified system was described later [100]. It contained an electron relay in addition to $Ru(bpz)_3^{2+}$, the electron donor and the microheterogeneous CH_4 formation catalyst. The principle of the first-reported system is indicated in Scheme 9.

The key to the success of the systems discussed above is probably the poor ability of $Ru(bpz)_3^+$ to reduce water to H_2. This particular property allows CO_2 instead of H_2O to be reduced, the selectivity of the noble metal catalyst (ruthenium, osmium) also being an important factor. At present the system is still of limited efficiency but it is certainly highly promising.

F. CONCLUSION AND OUTLOOK

The development of electrochemical systems based on molecular species for electrochemically reducing CO_2 has been spectacular over the past decade. Since the first reports on CO_2 electroreduction catalysed by porphyrins or phthalocyanines in 1977 [30,33,34], numerous transition metal complexes have been proposed by various research groups, providing a promising outlook toward photochemical fixation of CO_2. Until now, the reduction products have not been of great economic value (CO or $HCOO^-$), although some very recent results tend to indicate that more reduced C_1 molecules can also be obtained.

The search for more selective and probably more sophisticated catalysts is certainly very useful. It would of course be highly interesting to develop systems able to reduce CO_2 to C_2 products or to electro-incorporate reduced forms of CO_2 into cheap organic or inorganic substrates.

Another research line which shows considerable promise is the photo-assisted or completely photochemical approach. It is clear that multicomponent systems containing a photoactive centre, electron relays and/or molecular electrocatalysts in addition to possible microheterogeneous catalysts will be discovered. As for the photochemical cleavage of water, non-electrochemical systems will have to face the very difficult problem of the electron source. Ideally, it should be water itself that provides the electrons for the CO_2 reduction system with simultaneous evolution of O_2. If such systems can be developed in the future, they will bring artificial photosynthetic systems closer to natural photosynthesis.

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