Proc Indian Natn Sci Acad, **70, A,** No. 3, May 2004, pp.

ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE: A STATUS REPORT

M AULICE SCIBIOH AND B VISWANATHAN

Department of Chemistry, Indian Institute of Technology Chennai-600 036 (India)

(Received ; Accepted)

A status report on electrochemical reduction of CO_2 on metal cathodes with and without molecular catalysts is provided. Notable developments in this area of research have been systematically summarized. The various factors which influence the efficiency and selectivity of the CO_2 reduction process is critically evaluated and a rationale is evolved towards the choice of cathode materials, fabricational approaches, morphology of the electrode and various experimental parameters. The areas need attentions are identified and directions for further development are suggested.

Key Words : Electrochemical Reduction; Electrocatalysis; Activation of CO_2; Carbondioxide; Supporting Electrolytes; Cathode Materials; Molecular Catalysts; Transition Metal Complexes; Macrocyclic Ligands; Homogeneous Catalysis; Heterogeneous Catalysis

1 Introduction

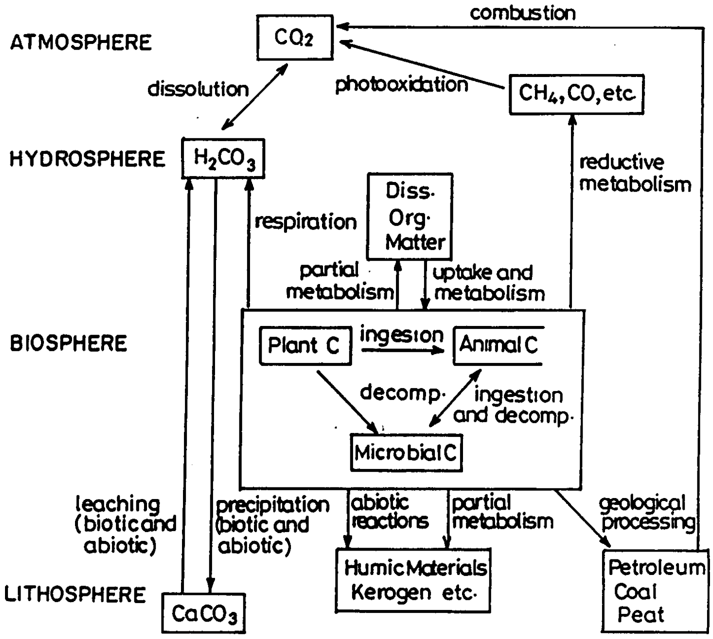
1.1 CO_2 Reduction: Relevance

Energy from the sun drives the earth's weather and climate, and heats the earth's surface: in turn, the earth radiates energy back into space. Atmospheric green house gases (water vapour, CO_2 and other gases) trap some of the outgoing energy, retaining heat somewhat like the glass panels of a greenhouse. Without this natural "greenhouse effect", temperatures would be much lower than they are now, and life as known today would not be possible. Instead, thanks to green house gases, the earth's average temperature is a more hospitable 60°F. However, problems may arise when the atmospheric concentration of greenhouse gases increases. Sources of CO_2 can be categorized in terms of the concentration of this material as high or low. Examples of the former include natural reservoirs, natural gas processing plants and facilities engaged in the production ethylene oxide, ammonia or hydrogen. The largest potential supply of CO_2, however, is from dilute sources that comprise various fossil fueled power plants (including coal, oil-and gas-fired facilities). Carbon dioxide is an intrinsic part of both inorganic and organic cycles, bridging the two (Scheme 1).

Since the beginning of industrial revolution in the second half of the 19th century, atmospheric concentrations of CO_2 have increased nearly 30% (Fig.1). The possible connection between anthropogenic CO_2 emission, the increasing CO_2 content of the atmosphere and the global climate has for some years been exhaustively investigated[1-5]. The 20th century's 10 warmest years all occurred in the last 15 years of the century. Of these, 1998 was the warmest year on record. The snow cover in the Northern Hemisphere and floating ice in the Arctic Ocean has decreased. Globally, sea level has risen 4-8 inches over the past century. Worldwide precipitation over land has increased by about one percent. The frequency of extreme rainfall events has increased throughout much of the United States. Increasing concentrations of greenhouse gases are likely to accelerate the rate of climate change.

Scientists expect that the average global surface temperature could rise 1-4.5°F (0.6-2.5°C) in the next fifty years, and 2.2-10°F (1.4-5.8°C) in the next century, with significant regional variation. Evaporation will increase as the climate warms, which will increase average global precipitation. Soil moisture is likely to decline in many regions, and intense rainstorms are likely to become more frequent. Sea level is likely to rise two feet along most of the U.S. coast. The observed changes in the global mean temperature between the years 1800-2000 is given in Fig. 2. Estimating the risks that would follow from a global climatic change and developing strategies for the prevention of further increase in the atmospheric CO_2 concentration are undoubtedly important tasks.

The transformation of CO_2 in to organic substances is a promising, long-term objective. It could allow the preparation of fuels and chemicals from the cheap and abundant carbon source. A number of different carbon



Scheme 1

Diagram of carbon cycle, showing movement of oxidized and reduced carbon species between the atmosphere, hydrosphere, bio-sphere and geo-sphere

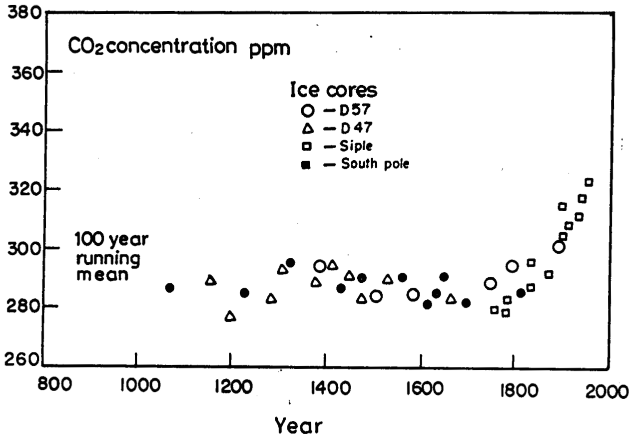


Fig. 1 Changing concentrations of CO_2 in the atmosphere over the past 1000 years. The measurements are taken from four Antartic ice cores and are combined with those from Mauna Loa, Hawaii. Note the rapid increase since about 1850. (Source: Intergovernmental panel of climate change)

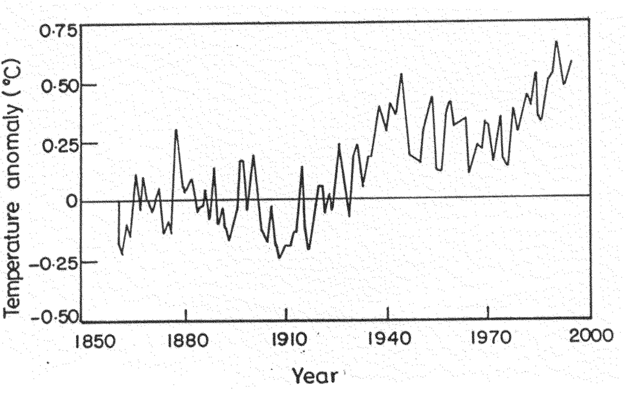


Fig. 2 Observed changes in the global mean temperature from 1800 to 2000. (Source: Intergovernmental panel of climate change)

compounds produced worldwide at the present time is approximately 50,000[6]. This large number of substances are produced from only a very few basic chemical raw materials, the source of carbon being almost exclusively fossilized matter, namely mineral oil, natural gas and coal. The fact that these resources are limited has led to a growth of scientific efforts to find alternative carbon sources, since the early 1970s. CO_2 has always attracted the greatest interest[7-13], as nature uses this compound so successfully as a synthetic building block in photosynthesis - the basis of life on earth. The carbon reserves on our planet in the form of CO_2 and CO_3^{2-} are for practical purposes inexhaustible, exceeding the carbon content of the deposits of fossil raw materials many times over.

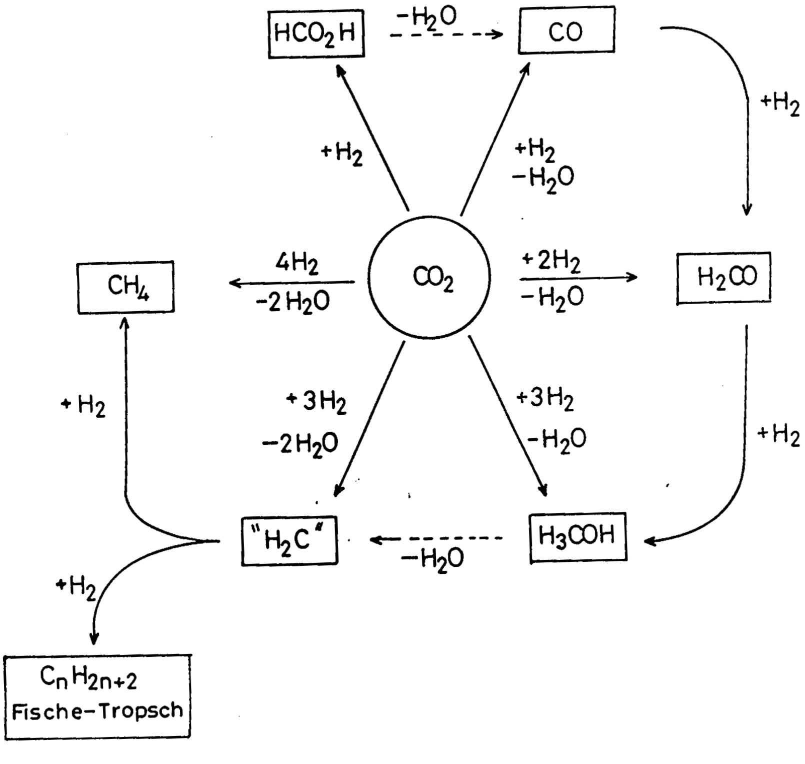
From the safety aspects, CO_2 is an ideal raw material, as can be seen from a comparison of its properties with those of the widely used C, starting compounds, carbon monoxide (CO) and phosgene ($COCl_2$) (Table I). For example, CO_2 is practically nontoxic, and can be stored, transported and handled without much difficulty.

CO_2 is already being used as a raw material in some industrially important chemical reactions[8], as shown in Scheme 2. Most current applications of CO_2 are based on its physical or physico-chemical properties[16,17]. The reduction equivalents required for the individual transformations can be made available by addition of hydrogen or by electron transfer processes. The important properties of CO_2 are given in Table II[23]. CO_2 is very stable, as illustrated by its standard free energy of formation ($\Delta G° = -394.359$ kJ/mol)[24]. CO_2 is the most oxidized form of carbon, and therefore the only chemical transformation at "normal" energies would be to reduce it. Upon transfer of one electron, the structure changes from linear to bent[25], which results in irreversible reduction. The qualitative molecular orbital energy level diagram[26] for CO_2 is given in Fig. 3.

Table I

Properties of Various C_1 Building Blocks

Factors	CO	$COCl_2$	CO_2
MAK Value	30 ppm	0.1 ppm	5000 ppm
Toxicology	Affinity for Hemoglobin 210 times that of O_2	War gas	Danger of asphysiation at 10 vol % in air
Environmental Hazard	Yes	High	Negative
Flammability	12 – 74 vol %	No	No
Boiling point	81 K	291 K	195 K (subl)
Storage	Only at < 3.5 Mpa	Very difficult	No problem
Transport	Gas bottles or tanks kg quantities	Possible	Gas bottles or tanks



Scheme 2

Reduction of CO_2 to provide sources for industrially important products

Table II

Selected Properties of CO_2

Point group	Dαh
Ground state	$1\Sigma_g^+$
Boiling point (°C)	-78.5
LUMO	$2\pi_u$
HOMO	$1\pi_g$
Bond length (Å)	1.16 (C-O)
Bond energy (eV)	5.453
Ionization potential (eV)	13.78
Electron affinity (eV)	-0.6
IR data (cm^{-1})	1320, 235, 668

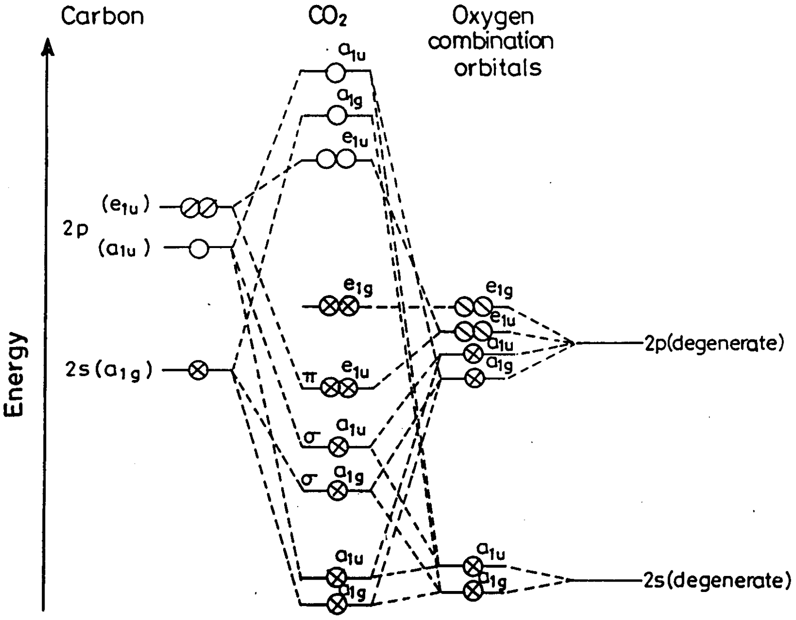


Fig. 3 Qualitative molecular orbital energy-level diagram for CO_2

1.2 Interaction of CO_2 with Transition Metal Centres

CO_2 is a typical linear triatomic molecule. The central carbon atom possesses sp hybridization and the C-O distance of 1.16Å, which is shorter than a C-O double bond involving an sp^2 carbon centre. The different electronegativities of oxygen and carbon lead to a negative polarization on the oxygen atom and a partial positive charge on the central carbon atom. Thus, CO_2 molecule exhibits several distinct positions that require specific electronic properties for possible coordination as shown in Fig. 4.

Transition metal carbon dioxide complexes may provide both structural and functional models for surface-bound intermediates in catalytic conversion processes. Particularly, in the past two decades, many such compounds have been identified. Although initially thought to be a poor ligand[27], CO_2 has demonstrated surprising versatility by exhibiting a great variety of coordination modes in metal complexes.

The early reports on the possibility of coordinating CO_2 to transition metal centers came from Vol'pin *et al.* in 1969[28] and Jolly *et al.* in 1971[29], but the information on the binding mode of the CO_2 ligand was limited at that time. It is clear from Fig. 4 that coordination of CO_2 results in a net transfer of electron density from the metal to the LUMO of the ligand if the complexation takes place via the double bond or the central carbon atom. The LUMO of the CO_2 is an antibonding orbital and therefore electron transfer should result in a weakened-C-O interaction. Furthermore, according to Walsh's rules[30], a bending of the linear CO_2 molecule similar to the bent structure of the radical anion CO_2 is expected[31]. The classification of bending modes in CO_2 metal complexes is shown in Fig. 5[32]. A detailed review

O ← Lewis Base → M ← C → M = electron rich
‖
C ← π-complexes → bond
(Dewar-Chatt-Duncanson) → suitablle orbitals
‖
O ← Lewis acid → M ← O → electron rich

Fig. 4 Reactive positions of the CO_2 molecule and the electronic properties of a transition metal centre required for complexation

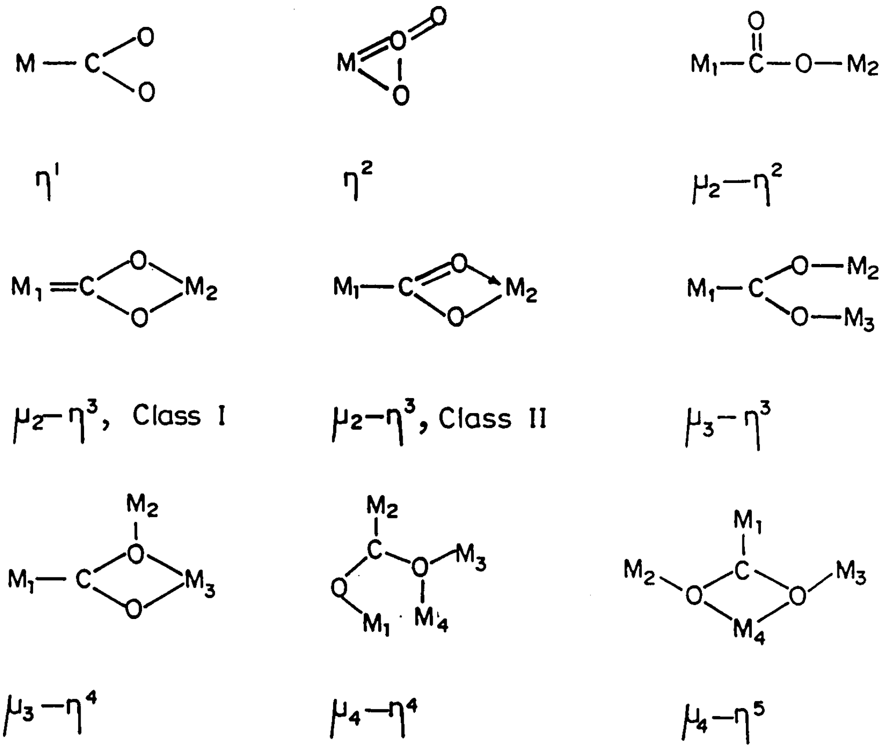


Fig. 5 Structural types of metal CO_2 complexes

of the synthesis, characterization and reactions of various types of CO_2 complexes are summarized by Gibson[32]. Different coordination modes of CO_2 to transition metal centres have been described in that paper. It is clear that CO_2 is in an "activated state" when the bonding involves the central carbon of CO_2. The activation is evident from the structural data like the bent OCO moiety and increased C-O distance and from spectroscopic data like low field shifts in ^{13}C-NMR and low frequency OCO vibration modes in IR spectral studies. The 'activation' is also reflected in the reactivity of coordinated CO_2.

CO_2 molecule also undergoes insertion reaction into the M-H bond, M-C bond, M-N bond, M-O bond, M-Si bond and M-P bond. The insertion reactions of CO_2 have been reviewed in the recent past by Pandey[33] and are discussed in the references cited therein. However, the precise relationship between these model compounds and their catalytic active analogues is not yet clear, and the structural and/or electronic properties of metal-CO_2 adducts that may be required for catalytic activity are not yet clearly understood[32].

1.3 Attempts at CO_2 Reduction

There are different ways to reduce CO_2 several of which are listed below. Examples are given of the various sources of energy used alone or in combination.

- *Radiochemical Method*

  General aspects in the radiation chemistry of CO_2 excitation are discussed by Boyd *et al.*[34]. The first report on radiochemical reduction of CO_2 by Getoff *et al.*[35] in aqueous media, using γ-radiation resulted in the product formation of HCOOH and HCHO.

$$CO_2 \xrightarrow{\gamma\text{-radiation}} HCOOH,\ HCHO \qquad \ldots(1)$$

Voss *et al.*[36,37] discussed the future role of nuclear energy and alternative sources of energy with regard to climate change and CO_2 problem. Komissararo *et al.* [38] calculated the steady state concentration of products from radiolysis of CO_2 by nuclear fission fragments.

- *Chemical Reduction* by metals, which occurs at relatively high temperatures[39]

$$2Mg + CO_2 \rightarrow 2MgO + C \qquad \ldots(2)$$
$$Sn + 2CO_2 \rightarrow SnO_2 + 2CO \qquad \ldots(3)$$
$$2Na + 2CO_2 \rightarrow Na_2C_2O_4 \qquad \ldots(4)$$

- *Thermo Chemically*[40]

$$CO_2 \xrightarrow[T>900^\circ C]{Ce^{4+}} CO + \tfrac{1}{2}O_2 \qquad \ldots(5)$$

- *Photo Chemically*[41,42]

$$CO_2 \xrightarrow{h\nu} CO,\ HCHO,\ HCOOH \qquad \ldots(6)$$

- *Electrochemically*[43]

$$CO_2 + xe^- + xH^+ \xrightarrow{eV} CO,\ HCOOH,\ (COOH)_2 \qquad \ldots(7)$$

- *Biochemically*[44,45]

$$CO_2 + 4H_2 \xrightarrow{\text{bacteria}} CH_4 + 2H_2O \qquad \ldots(8)$$

The bacteria *Methanobacterium thermoautotrophicum* can be immobilized in affixed bed or on hollow fibers, and feeding stoichiometric ratios for the reaction attains 80% of the theoretical yield.

- *Biophotochemically*[46,47]

The "bio" part of the energy consists in catalysis and information content of an enzyme.

$$CO_2 + \text{oxoglutaric acid} \xrightarrow{h\nu} \text{isocitric acid} \qquad \ldots(9)$$

In studies of this reaction[46,47], the enzyme was isocitrate dehydrogenase, $Ru(bpy)^{2+}_3$ was used as photosensitizer, *d,-1*-dithiothreitol was the electron donor, and ferredoxin-$NADP^+$ reductase was included for recycling NADPH.

- *Photo electrochemically*[48]

$$CO_2 + 2e^- + 2H^+ \xrightarrow[\text{eV, semicond}]{h\nu} CO + H_2O \qquad \ldots(10)$$

Other products than CO are possible, and their distribution and yields depend on many factors[49]

- *Bioelectrochemically*[50]

$$CO_2 + \text{oxoglutaric acid} \xrightarrow[\text{eV, methylviologen}]{\text{enzyme}} \text{isocitric acid} \qquad \ldots(11)$$

- *Biophotoelectrochemically*[51]

$$CO_2 \xrightarrow[\text{eV, methylviologen}]{h\nu\text{. enzyme, p-1nP}} HCOOH \qquad \ldots(12)$$

when the enzyme is formate dehydrogenase.

Among various possible approaches, the electrochemical reduction of CO_2 seems to be an attractive method for the removal and conversion of CO_2 [52-54].

2 Electrochemical Reduction of CO_2

The electrochemical reduction of CO_2 is still of great interest in the fields of theoretical and applied electrochemistry. 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 $E^{\circ\prime}$ values given below [55,56], 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 processes: As expected, the redox potentials become less and less negative as the reaction involves multielectronic pathways. In contrast, the value of the $CO_2/CO_2^{\cdot-}$ redox potential is -2.21V /(SCE)[55-56], making the monoelectron reduction mechanism highly unfavourable.

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^{\circ\prime} = -0.52\ V \quad \ldots(13)$$
$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad E^{\circ\prime} = -0.61\ V \quad \ldots(14)$$
$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E^{\circ\prime} = -0.48\ V \quad \ldots(15)$$
$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^{\circ\prime} = -0.38\ V \quad \ldots(16)$$
$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^{\circ\prime} = -0.24\ V \quad \ldots(17)$$

The electrochemical approach has the advantage that water can be used as the proton source[57]. In addition, electrochemical CO_2 reduction can be carried out at room temperature. The main concurrent reaction in aqueous solutions with CO_2 reduction is hydrogen evolution[58-60]. Depending on the electrode material used and the experimental conditions adopted[58-60], different products of CO_2 reduction were obtained[60]. However, if this approach is to be considered seriously, it is important to develop ways to reduce CO_2 electrochemically with high efficiency and selectivity and at high current densities.

Therefore, the various factors affecting the reduction of CO_2 will be examined. The strategies used to enhance the reduction of CO_2 are based on varying one or more of these factors; in much of the published works, the advantage of using a particular combination of, for example, solvent, electrolyte, and electrodes is not clear, and the product analysis is not always complete. By 'enhancement' we mean either improved yields, be they for energy or chemical conversion, or steering the reaction on a desired path resulting in a certain distribution of products. For this purpose, however, one must be acquainted with some of the properties of CO_2 relevant for its reduction.

2.1 Thermodynamics of CO_2 Reduction

A summary of the thermodynamics of CO_2 reduction to one-carbon fragments in aqueous solution under basic and acidic condition is shown in the following Scheme 3[61]. A negative potential indicates that the reduced form of the couple is a better reducing agent than H_2, and conversely, a positive value means that the oxidized form is a better oxidizing agent than the proton at the specified pH. In acidic solution, reduction of CO_2 to either HCOOH or CO is slightly endergonic with respect to the H_2/H^+ redox couple, while reduction to methane is actually spontaneous.Though, various reductions are accessible at reasonable potentials, their kinetic barriers are quite severe, consequently, substantial overpotentials can be incurred at the electrode surface. In Table III, the free energy changes and the standard redox potentials for several reactions of the reduction of CO_2 at pH=O are cited.The reduction potentials for various radicals of interest for reduction of CO_2 obtained through thallium titration[67] are given in Table IV[65-66].

On the basis of tabulated thermodynamic data, one may calculate the changes in redox potentials with temperature in the range 0-200°C for C (graphite), CO, HCOOH, HCHO, CH_3OH and CH_4 for the reaction:

$$CO_{2\ (aq.un)} + me^- + mH^+ \rightarrow \text{Product} + n\ H_2O_{(l)} \quad \ldots(18)$$

The thermodynamic values for the aqueous unionized (aq.un) CO_2 were chosen, since it is CO_2 and not the carbonate ion that is reduced[67]. The reaction is a reduction protonation and not hydrogenation[68]. The variation of redox potential E with temperature was calculated according to the equation[61],

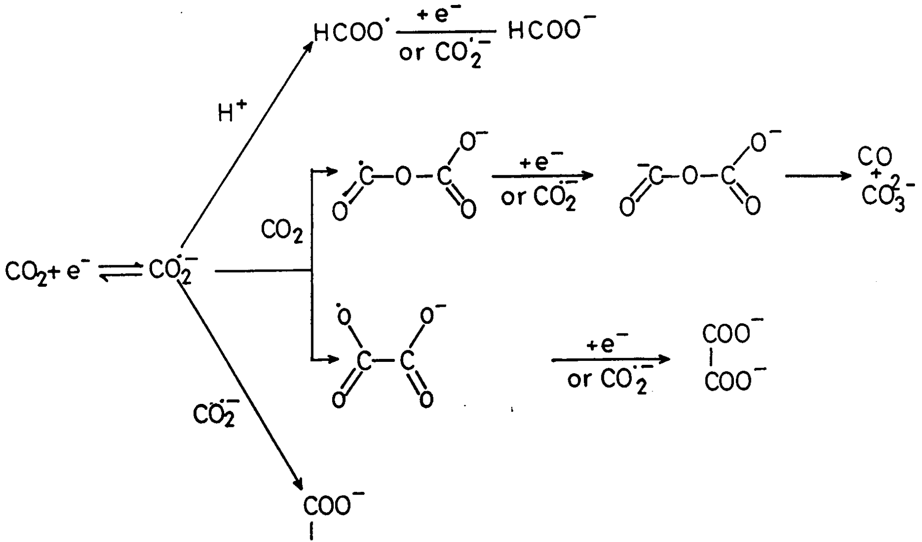
$$E(T) = \frac{-\Delta G(T)}{nF} = -\frac{[\Delta H(T) - T\Delta S(T)]}{nF} \quad \ldots(19)$$

where G is the Gibbs free energy, and the variations of the enthalpy (H) and entropy (S) with temperature (T) are approximated by the expressions:

$$\Delta H(T) \approx \Delta H^\circ + \Delta C^\circ_p\, \Delta T \quad \ldots(20)$$

$$\Delta S(T) \approx \Delta S^\circ + \Delta C^\circ_p\, \Delta(\text{InT}) \quad \ldots(21)$$

Where, C_p is the specific heat at constant pressure, and the superscript° means standard values. Whenever the values for the aqueous form were not available, the values for the gas phase were chosen. The results of this approximate calculation of redox potential are shown in Fig. 6, which indicate that temperature is one of the factors influencing the outcome of reaction. At



Scheme 3
Reaction mechanism of reduction of CO_2

Table III

Free Energy of Reaction, at 273 K, and Standard Potentials for a $CO_{2\,(aq.un)} + ne^- + nH^+_{(aq.un)}$ = *Products* + $qH_2O_{(l)}$ [a,b]

Product	State	ΔG (kJ/mol)	E (V)[c]
CO	g	11.68	-0.061
	aq un	28.95	-0.150
HCOOH	l	24.63	-0.128
	aq	13.68	-0.071
	aq ion	34.98	-0.181
C	graphite	-88.28	0.229
HCHO	g	46.32	-0.120
	aq un	148.85	-0.386
CH_2OH	l	-17.42	0.03
	g	-13.11	0.023
	aq un	-26.46	0.046
CH_4	g	-139.00	0.180
	aq un	-122.61	0.159
$(COOH)_2$	aq ion 1	98.06	-0.508
	aq ion 2	73.62	-0.382
CH_3COOH	l	-92.20	0.119
	g	-76.30	0.099
	aq un	-98.76	0.128
	aq ion	-71.61	01.093
CH_3CHO	l	-67.55	0.07
	g	-68.29	0.071
C_2H_4	g	-108.41	0.094
	aq un	-95.20	0.082
C_2H_5OH	l	-114.21	0.099
	g	-107.92	0.093
	aq un	-121.07	0.105
$(CH_3)_2O$	g	-52.02	0.045
$(CH_2OH)_2$	l	-262.51	0.227
C_2H_6	g	-209.38	0.155
	aq un	-193.57	0.143
CO_2	aq		-1.84[c]
			-1.9[c-e]

[a] aq un, aqueous not ionized
[b] Ref. 62 & 24
[c] Ref. 63
[d] value refers to $CO_2(g)$ as starting substance
[e] Ref. 64

Table IV

Thermodynamic Data for Some Radicals of Interest for CO_2 *Reduction*

$RO^{\cdot -}$	E° ($RO/RO^{\cdot -}$)	PK[a]	E° ($RO,H^+/ROH$)[b]
$CH_2O^{\cdot -}$	-1.81	10.71	-1.18
$CH_3CHO^{\cdot -}$	-1.93	11.51	-1.25
$(CH_3)_2CO^{\cdot -}$	-2.1	12.03	-1.39
$CO_2^{\cdot -}$	-1.9	1.4	-1.82

[a] Ref. 65
[b] E° ($RP,H^+/ROH$) = E° ($RO,H^+/RO^-$) – 0.0592 $pK._{ROH}$
[c] Ref. 66

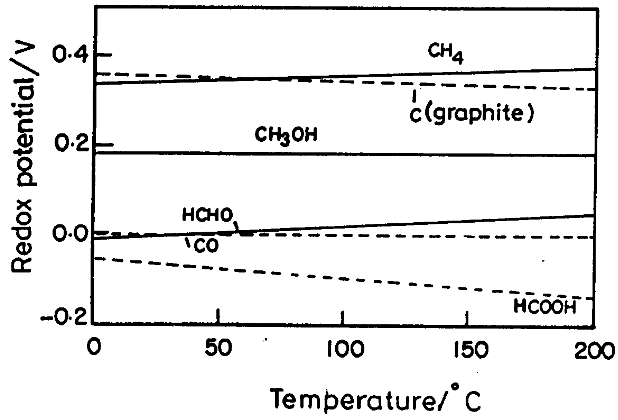


Fig. 6 Change with temperature of the redox potential for reduction of CO_2 to C_1 species

low temperature, the production of CO is less favoured electrochemically than that of formaldehyde and the reverse is true at high temperatures. From Table III, it is clear that none of the reactions of reduction of CO_2 requires large amounts of energy except the formation of the CO_2^- radical. The electrochemical reduction of CO_2 at high temperatures was attempted[69] and the reaction was performed in molten salts (chloride or carbonate eutectic). Advantage is taken of both increased temperature and large potential window of the eutectics [e.g., 3.6 V for (Li, K) Cl eutectic]. At 873 K, the reduction of CO_2 starts at -0.6 V/Ag and reaches 12% efficiency at 1073K. Corrosion is, however, a severe problem and was considered responsible for observed Faradic yields in excess of 100%.

2.2 Mechanism of the Reduction of CO_2

2.1.1 In Aqueous Solvents

Jordan and Smith[70], Sawyer *et al.*[71] Paik *et al.*[72], Ryu *et al.*[73] and Aylmer – Kelly *et al.*[74] have proposed reaction mechanisms for the electroreduction of CO_2 in aqueous solutions. Most workers have assumed the intermediate to be the anion radical CO_2^- formed by the initial single electron transfer.

$$CO_2 + e^- \rightarrow CO_2^- \qquad \ldots(22)$$

Paik *et al.*[72] then proposed the following steps

$$CO_{2ads}^{\bullet -} + H_2O \rightarrow HCO_{2ads}^{\bullet -} + OH^- \qquad \ldots(23)$$

$$HCO_{2ads}^{\bullet -} + e^- \rightarrow HCO_2^{\bullet -} \qquad \ldots(24)$$

As an alternative, Ryce, Anderson and Eyring suggested that the eqs. (22), (23) could take place as a single step.

$$CO_2 + H_2O + e^- \rightarrow HO_{3ads} + OH^- \qquad \ldots(25)$$

where, $CO_2.H_2O$ mean hydrated CO_2 and HCO_{2ads} stands for the reaction intermediate (formate radical) adsorbed on the mercury cathode.

It is difficult to differentiate the three-step mechanism from the two-step one. The involvement of CO_2^- as an intermediate is supported by its demonstrated existence in the product of reaction of UV radiation with CO_2[75] and of γ-irradiation of sodium formate crystals[76].

Paik *et al.*[72] provided evidence for the existence of the HCO_{2ads} as reaction intermediate from galvanostatic charging curves ($\theta \sim 1$). Modulated specular reflectance spectroscopy, indicated the presence of CO_2^- as an intermediate in the electrochemical reduction of CO_2[74] The coverage of the intermediate calculated from the optical data corresponded approximately to 0.02 of a monolayer[74]. Low CO_2^- coverage was also indicated by photoelectrochemical measurements[78]. On the basis of the optical data, Aylmer - Kelly *et al.*[74] suggested that no adsorbed intermediates are present in any appreciable amount and concluded that the reduction mechanism involves eqs. (22) to (24) but the intermediates are free in solution. This view is also consistent with the fact that the electrode is so negatively charged at the highly cathodic potentials involved, that the existence of CO_2^- species on the cathode as a reaction intermediate is difficult. From the calculation of the maximum flux of a hydrogen ion supported by dissociation of a water at neutral pH values, Aylmer - kelly *et al.*[74] concluded that the predominant reaction of CO_2^- must be with a water and not with a hydrogen ion.

In acidic solutions this process [eqs. (22) to (24)] occurs in parallel with the reduction of H_3O^+ ions. The hydrogen atoms formed react in a branching mechanism either with H_3O^+ and electrons to yield H_2, or with CO_2 to eventually form HCOOH. The following reaction sequence has been proposed[74].

$$CO_2 + e^- \overset{\text{r.d.s}}{\rightarrow} CO_2^{\bullet -} \qquad \ldots(22)$$

$$CO_2^- + H_2O \rightarrow HCO_2 + OH^- \qquad \ldots(23)$$

(or)

$$CO_2^- + H^+ \rightarrow HCO_2 \qquad \ldots(26)$$

$$H^+ + e^- \overset{\text{r.d.s}}{\rightarrow} H_{ads} \qquad \ldots(27)$$

$$H_{ads} + CO_2 \rightarrow HCO_2 \qquad \ldots(28)$$

(or)

$$H_{ads} + H^+ + e^- \rightarrow H_2 \qquad \ldots(29)$$

$$HCO_2^{\bullet} + H^+ + e^- \rightarrow HCOOH \qquad \ldots(30)$$

Because of the high cathodic potential involved in the direct reduction of CO_2 to HCOOH, in low pH the latter reaction proceeds at a negligible rate compared with that of hydrogen evolution. Under these conditions, formic acid is produced (with a 10% current efficiency at pH 1.4) via the hydrogen atom route [eqs. (27) to (30)] and the Tafel lines are same in CO_2 and N_2 saturated solutions.

Other mechanisms involving the formation of amalgam followed by the reaction of CO_2 and H_2O with the amalgam, a two electron transfer in one step[71] to give CO_2^{2-} or positively charged reactant intermediates. (eg. HCO_2^+), were rejected by Paik *et al.*[67] as being inconsistent with the experimental data. The general mechanism of the reduction of CO_2 is shown in Scheme 3.

2.2.2 In Aprotic or Partially Aprotic Solvents

In aqueous solutions, the electroreduction of CO_2 leads to the formation of formic acid; except for unconfirmed reports claiming that CO_2 can be electrolytically reduced to malate or glycolate[79,80], the formation of carboxylic acids other than formic acid has not been reported. In contrast, in aprotic solvents the reduction of CO_2 to oxalate ion is possible since the protons necessary for the formation of formic acid are lacking. The electrochemical dimerization of CO_2 may occur according to the following scheme[81].

$$CO_2 + e^- \rightarrow CO_{2ads}^{-} \qquad \ldots(22)$$

$$CO_{2\,ads}^{-} + CO_{2ads}^{\cdot -} \rightarrow (COO)_2^{2-} \qquad \ldots(31)$$

A parallel reaction leading to the formation of CO and carbonate ion may also take place[79,80].

Another competing process may occur when traces of water are present[78].

$$CO_{2ads}^{-} + H_2O \rightarrow HCOO^- + OH_{ads} \qquad \ldots(33)$$

$$OH_{ads} + CO_{2ads}^{-} \rightarrow HCO_3^- \qquad \ldots(34)$$

The reaction path is influenced by the cathode material and by the solvent. When the electrodes strongly adsorb CO_2, as with Pt for example, reaction given in eq. (32) occurs predominantly. Weakly nucleophilic aprotic solvents such as propylene carbonate and acetonitrile, favour eq. (31). The following compounds have been detected under partially aprotic conditions[81] glyoxylic, glycolic, tartaric, malic and succinic acids. They can be formed according the Scheme 4.

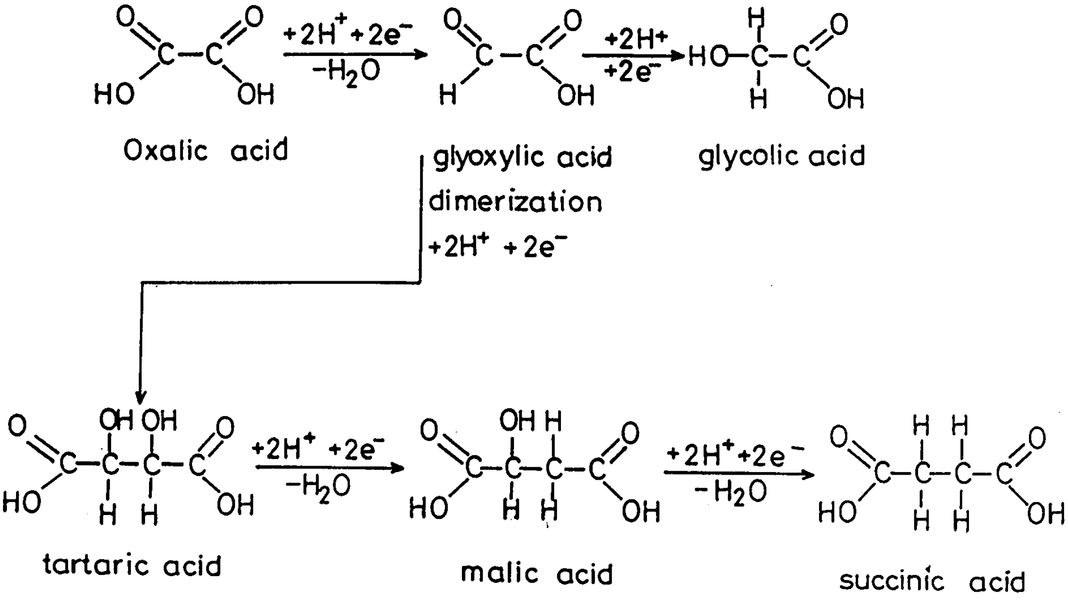
2.3 Solubility

Next to temperature, another equilibrium property that must be taken into consideration is the solubility of CO_2 in various solvents. The solubility of CO_2 at 1 atm, expressed as the Bunsen co-efficient α, in water and ethanol obeys the equation

$$\alpha = A_1 - A_2t + A_3t^2 \qquad \ldots(35)$$

where, 't' is the temperature in °C, and A_1, A_2 and A_3 are co-efficient dependent on the solvent for water, $A_1 = 1.7326$, $A_2 = 0.066724$, and $A_3 = 0.0012394$; for ethanol, $A_1 = 4.3294$, $A_2 = 0.09426$ and $A_3 = 0.001239$. The variation of solubility of CO_2 plotted as a function of temperature for several solvents relevant to electrochemistry are shown in Fig. 7.

In all cases, the solubility decreases with increasing temperature, but for most organic solvents the solubility is much higher than in water, and unrelated to their dielectric constant. The solubility of CO_2 in dimethyl sulfoxide (DMSO) and acetonitrile (CH_3CN) is 4 times that in water, in dimethyl formide (DMF) 20 times and in propylene carbonate 8 times. (The exact numbers may differ; *cf*: reports of 0.04 M[82] with 0.14 M for CO_2 in acetonitrile[83])[84]. For practical applications the high solubility in and diffusivity through plastics must also be considered; for example the solubility of CO_2 in rubber is quite remarkable, *ca.*, 70 mlCO_2/100 ml



Scheme 4
Reduction of CO_2 under partially aprotic conditions

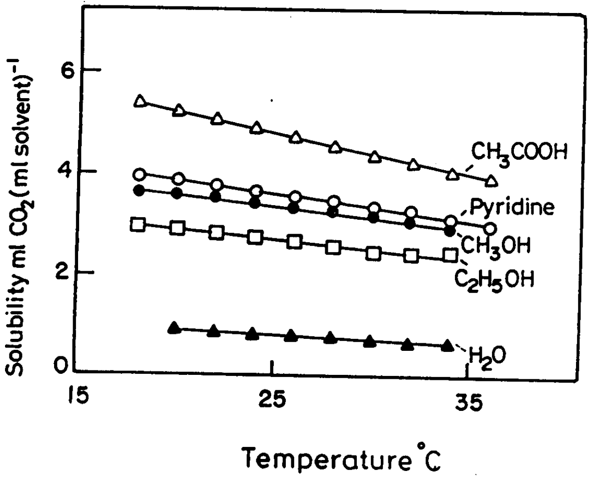


Fig. 7 Variation of the solubility of CO_2 with temperature for several solvents used in electrochemistry

rubber (the value may vary according to the quality of the rubber)[85].

Chemical character of the solvent is an important factor in determining the course and yield of the reaction. The work of Taniguchi *et al.*[42] showed that protophilic solvents such as dimethyl formamide or dimethyl sulfoxide, decrease the hydrogen evolution in the course of the competition between CO_2 and H^+ for electrons at illuminated semiconductor electrodes photophobic solvents such as propylene carbonate or acetonitrile, favour the hydrogen evolution during the reaction. This is illustrated by the fact that the catalytic reduction of CO_2 to formic acid occurs on modified electrodes in dimethylformamide, but not in acetonitrile[86].

Solubility is strongly dependent on pressure, and it can be approximated by Henry's law, as shown in Fig. 8. It is noticed that the proportionality constant depends on temperature and is different for different solvents. That means that in some instances a reversal in the ordering of solvents according to CO_2 solubility can occur.

The effect of pressure on solubility is felt strongly by the electrochemical potential. For instance, studies were made on semiconductor electrodes to investigate the effect of pressure[87] and were found that the Faradic efficiency was low and decreased with current density. Later studies demonstrated the use of gas-diffusion electrodes for the high rate electrochemical reduction of CO_2[88] in an attempt to increase current density by increasing local pressure, and the current density for formate production reached 50 mA/cm^2 on Pb impregnated electrodes[89]. Moreover, for electrochemical applications, the stability domain of the solvent is important and must be co-related with the properties of the particular electrode and supporting electrolytes employed.

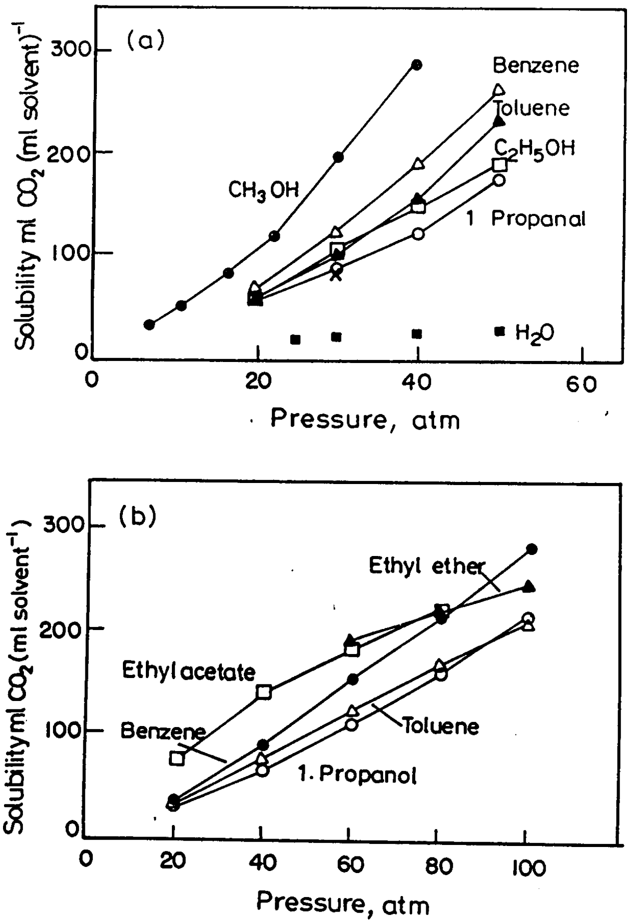


Fig. 8 Variation of solubility of CO_2 with pressure for several solvents at T = 293K and 333K

2.4 *Electrolytes*

The electrolyte medium, which consists of solvent and the supporting electrolyte, exerts a major influence on the nature of the electrochemical processes. The chemical properties of the electrolyte medium affect the electrochemical reaction mechanism in the same way solvents affect the normal reaction chemistry[90]. At the earlier stages, the effect of supporting electrolyte has not been studied intensively; the supporting electrolyte is regarded only as a component to give ionic conductivity. Later as in ref.[91] it is understood that the supporting electrolytes influence both the solubility and mechanism of reaction in the course of reduction of CO_2. The exact mechanism of dissolution of CO_2 is not fully understood[19]. For example, the solubility of CO_2 in H_2SO_4 solution goes through a minimum at a concentration of *ca*. 38 m, while in $HClO_4$ it pass through a maximum at a concentration of *ca*. 10 m[92]. The solubility of CO_2 in $Fe(OH)_2$ and Prussian Blue solutions increase over that in pure water[93]. This might be the explanation to the observed increase in current efficiencies for CO_2 conversion at illuminated p-silicon electrodes modified with Prussian Blue[92] or in more complex systems using the approach of homogeneous/heterogeneous catalysis[94,95]. Among common salts, solutions of $NH_4HB_2O_4$, $Na_4B_4O_7$, $NaBO_2$, Na_3PO_4. $12H_2O$ and Na_4 $P_2O_710H_2O$ dissolve more CO_2 than pure water[93].

Although, the effect of solutes on the solubility of CO_2 is well documented and moderately used, their effect as "catalysts" has been less used. Murata and Hori[96] reported the effect of alkali metal cations on the product distribution as caused by changes in the double layer structures, and Bockris *et al.*[97-99] reported the effect of tetralkylammonium ions. Tanighchi *et al.*,[99] showed that ammonium ions have a catalytic effect for the reduction of CO_2 on semiconductor electrodes in nonaqueous media. In spite of the electrode corrosion, the effect of electrolytes on current efficiency for the CO_2 reduction at semiconductor electrodes and product distribution were studied also in aqueous media[100]. It was shown that the alkali carbonates favoured formation of formate. Tetraethylammonium pechlorates suppressed H_2 evolution better than alkali carbonates, phosphates or sulfates. Hori *et al.*[101] investigated the influence of anions and electrolyte concentration on the reduction of CO_2 on copper electrodes. The salts investigated were KCl, $KClO_4$, K_2SO_4 and K_2HPO_4. It was not clear whether the differences observed in product distribution and yields are a consequence of changes in the composition of the electrolyte, pH or electrolysis potential. The main conclusion was that by changing one or more of the factors, the product distribution could be changed. The products reported are CH_4, C_2H_4, C_2H_5OH, PrOH, CO, $COOH^-$ and H_2.

For the reduction of CO_2 in aqueous media, water itself is an electrolyte, and it was shown to exert notable effects on the course of the reaction[102].

2.5 Need for Catalysis

The reduction of CO_2 necessitates a source of energy. This energy can be thermal, luminous, nuclear, chemical or electrical or combinations thereof. Some forms of energy require at least one carrier or mediator that will convey the energy to CO_2. For instance, in the case of visible and near-UV light, mediators are photosensitizers or semiconductors; in the case of chemical energy, there are bio-systems that result in methanation. As seen in Table III, none of the reactions requires a huge amount of energy, nor do any of these reactions have a high standard potential. Some are even favoured over hydrogen evolution. The problem consists in the Manichean character of the reduction of carbon dioxide. On one hand, CO_2 competes with hydrogen for electrons and on the other hand, most of the reduction requires protons. Therefore, the problem is two fold: to transfer the electrons to CO_2 instead of protons, and after convincing them not to go to the protons, to labialise CO_2 sufficiently to receive them. In electrochemical terms, the reduction of CO_2 can be catalyzed either positively, in the sense that the overpotential is reduced, and/or the currents increased, or it can be catalyzed negatively, in the sense that competing reaction are discouraged. As is often the case in electrochemistry, the nature of the electrodes plays an important role in the system.

2.6 Reduction of CO_2 on Metal Cathodes

Large number of recent papers dealing with the electrochemical reduction of CO_2 is of both fundamental and preparative interest. As seen in Table V, the number of papers published on the electroreduction of CO_2 shows the spate of research on this field is due to the promising results of electrochemical approach, which can be applied on the industrial scale. Number of these procedures is currently being patented. All these electroreduction techniques had to overcome the difficulty of finding electrodes with both a high electrocatalytic activity and a satisfactory lifetime.

The reaction of electroreduction of CO_2 implies both protons and electrons, and therefore hydrogen evolution must be discouraged. The nature of the metal affects not only the yield, but also the distribution of products. One of the ways of doing this is to employ electrodes with high hydrogen overpotential. An alternative approach was also proposed in which the two processes are separated by using a Pd membrane that acts as a hydrogen reservoir[104]. Also, given the relatively low solubility of CO_2 in aqueous solutions, methods for improving the solubility of CO_2 had to be found. A possible solution to this problem is to perform the electroreduction at high pressures or in non-aqueous solutions. The electrocatalysis of CO_2 reduction at metallic electrodes in aqueous and non-aqueous solutions was investigated, and the results are summarized in Table VI. Table VI illustrates also the importance of the solvent on the product distribution.

Table V

Number of Papers Published in the Last Two Decades on the Electrochemical Reduction of CO_2

Year	Number of Papers Published
1982	20
1985	25
1986	28
1987	28
1988	27
1989	22
1990	29
1991	32
1993	33
1994	58
1995	59
1996	7
1997	20
1998	20
1999	15
2000	8
2001-till date	8

Table VI

Influence of the Solvent and Electrode on the Reaction Mechanism

Reaction	**Cathode**	**Solution**
$CO_2 + e^- \rightarrow CO_2^{\cdot -}$	All	All
$CO_2^{\cdot -} + H^+ + e^- \rightarrow HCOO^-$	In, Pb, Hg	H_2O
$CO_2^{\cdot -} \rightarrow CO^{\cdot} + O^{\cdot -}$		
$CO + O^{\cdot -} + H^+ + e^- \rightarrow CO + OH^-$	Zn, Au, Ag	H_2O
$CO_2^{\cdot -} + CO_2^{\cdot -} \rightarrow (COO)_2^{2-}$	Pb, Tl, Hg	Non-aqueous
$CO_2^{\cdot -} + CO_2 + e^- \rightarrow CO + CO_3^{2-}$	In, Zn, Sn, Au	Non-aqueous

To reduce CO_2 with high selectivity, high-energy efficiency and high reactivity, it is essential to evaluate various factors, which influence the course and products of the CO_2 electroreduction. Three kinds of electrodes are currently being employed: (i) bulk metal electrodes with appropriate electrocatalytic activity (ii) chemically modified electrodes (iii) metal electrodes in the presence of electrocatalysts dissolved in the supporting electrolyte. Bulk metals are considered suitable from the electrocatalytic standpoint if they have the ability to lower the overpotential while maintaining high current efficiencies and high current densities (>100 mA / cm^2).

Several classification systems have been used to systematize the extensive data accumulated in CO_2 -related synthetic work[105-109]. Most of these classifications are solely based on the nature of the main product obtained in the electrochemical synthesis. Four classes of metallic electrodes in aqueous supporting electrolytes and three classes for non-aqueous media can be distinguished[106-109]. Thus, in aqueous solution (i) metallic In, Sn, Hg and Pb are selective for the production of formic acid, (ii) metallic Zn, Au and Ag produce CO, (iii) metallic Cu exhibits a high electrocatalytic activity for the formation of hydrocarbons, aldehydes and alcohols, while (iv) metallic Al, Ga and Group VIII element (except Pd) show low electrocatalytic activity in CO_2 electroreduction[106-108].

In non-aqueous supporting electrolytes (i) on Pb, Tl and Hg the main product is oxalic acid[105], (ii) On Cu, Ag, Au, In, Zn and Sn, CO and carbonate ions are obtained [105,107,109], while Ni, Pd and Pt are selective for CO formation; and (iii) Al, Ga and Group VIII elements (except Ni, Pd and Pt) form both CO and oxalic acid[107].

Additional classification criteria for the processes occurring in CO_2 electro-reduction based on both the electrocatalytic properties of the electrode material and the nature of the supporting electrolyte would allow a better systematization of the multitude of reactions and would provide more insight into the mechanisms controlling the phenomena.

In the early seventies, the difference between the electrocatalytic behaviours of electrodes made of sp group metals and of d group metals, respectively[110-122], was recognized as an important aspect in determining the selectivity of electrode processes. Thus, when used in aqueous supporting electrolytes, sp group metal cathodes, such as Hg, In, Sn and Pb favoured the electroreduction of CO_2 to formic acid[110-113,119], while on d metals (eg. on Pt and Pd) CO was formed as the main product[121,123]. Another typical d group metal, Ru, was found to exert favourable electrocatalytic properties for the preparation of various compounds such as hydrocarbons (methane and ethylene), alcohols (methanol and ethanol) as well as formaldehyde[124-127].

In contrast, the same groups of metals behaved differently in non-aqueous supporting electrolytes: On sp group metals (Tl, Pb and Hg) oxalic acid was selectively formed, on several d group metals (Fe, Cr, Mo, Ti and Nb) oxalic acid and CO were the main products, while on several sp group metal electrodes (In, Sn, Cd, Zn, Cu, Ag and Au) and d group metal electrodes (Pd, Pt and Ni) CO was mainly formed[106,107,128,129-131].

This discussion of the electrochemical reduction of CO_2 will consider both the importance of the cathode metal and that of the solvent. Therefore, this part of discussion comprises two sub-sections, according to the type of electrodes used as the cathode material (sp and d group metals). Given the influence of the solvent on the nature of the products, in each section separate subsections are dedicated to work in aqueous and in non-aqueous media respectively. This systematization is similar to that already adopted by Jitaru *et al.*[108b] however, considerable progress has been made in this area over the last few years and therefore it sems appropriate to provide relevant updation.

2.6.1 Electrochemical Reduction of CO_2 on 'sp' Group Metals

As per the classification pattern of Kita[114], the sp group metals include the principal group metals of the periodic table and the transitional metals with completely filled d^{10} orbitals; that is, the metals with a d electronic configuration: Zn, Cd, Hg, Cu, Ag and Au. The results of significant investigations are given in Table VII.

- In 1980, Royer[132] has employed Zn electrodes in aqueous sodium bicarbonate electrolyte and obtained HCOOH. Later, Cohen and Jahn[133] improved Royer's methods by using Zn amalgam cathodes. Formic acid with current efficiencies (rf) up to 88.6% was obtained. Ehrenfield[134] further raised the rf to 95% by employing divided cell equipped with Zn amalgam vs. Pt electrodes, in the presence of ammonium bicarbonate supporting. electrolyte. Fischer and Prziza[135] obtained fair yields of HCOOH on Zn amalgam and Pb cathodes under pressurized electrolysis CO_2 (5-50 atm).
- Rotating amalgamated Cu cathodes[131] as well as Pb amalgam[136] were found to be efficient for the HCOOH formation. Watanabe *et al.*[137,138] have investigated the electrocatalytic activity of Cu-based alloys, such as Cu-Sn and Cu-Zn in addition to elemental Cu, Sn and Zn cathodes at low temperatures of 275 K.
- Ishimaru *et al.*[139] recently investigated the highly selective reduction of CO_2 to C_2 compounds such as CH_3CHO, C_2H_5OH and C_2H_4 on Cu-Hg alloy electrodes by employing pulsed electroreduction. The Faradic efficiencies of C_2 compounds produced on Cu-Ag alloy electrodes were varied with the atomic ratio of Cu and Ag. The total rf for C_2 compounds was 54.2% for the pulsed reduction on a Cu Ag alloy electrode (Cu/Ag = 28/72) with an anodic bias of Va = -0.4V and a cathodic bias of V_c = -2.0V vs Ag/AgCl. It was found that the formation of an oxide layer on Cu and the desorption of intermediates on Ag under anodic bias were key factors for the product selectivity. The products were found to be formic acid, methanol and CO.
- Noda *et al.*[128,110] found that in addition to Hg and Pb, metallic In and Sn were employed for the selective production of HCOOH. It was found that metallic Al and Ga exhibited no electrocatalytic activity towards CO_2 electroreduction. In 1983, Kapusta[140] and Hackerman employed In and Sn electrodes to produce HCOOH with 90% faradic efficiency.
- Ito *et al.*[112] reported the electrocatalytic activity of various sp group metals for the synthesis of formic acid. In and Cd with a medium value of the overpotential for the hydrogen evolution reaction, were employed as cathode in a divided electrochemical cell. In aqueous carbonate solution at 298 K, HCOOH was formed (rf) 70-80% with a current density from 5-10 mA/ cm^2. It not only catalyses the reduction of CO_2, but also inhibited

Table VII

Summary of Metal Cathodes Employed for Electroreduction of CO_2

Metals	Products	
	Aqueous medium	Non-aqueous medium
	sp group metals	
Cu, Zn, Sn	HCOOH	-
In, C, Si, Sn, Pb, Bi, Cu, Zn, Cd, Hg	HCOOH, CO, hydrocarbon	-
In, Sn, Pb, Cu, Au, Zn, Cd	-	Hydrocarbon, CO, CO_3^{2-}
In, Sn, Au, Hg	-	CO
In, Tl, Sn, Pd, Pd, Zn, Hg	-	Oxalic acid
	d group metals	
Ni, Pt	-	CO, CO_3^{2-}
Ni, Pd, Rh, Ir	HCOOH, CO	-
Fe, Ru, Ni, Pd, Pt	Hydrocarbon	-
Ti, Nb, Cr, Mo, Fe, Pd	-	Oxalic acid
Mo, W, Ru, Os, Pd, Pt	MeOH	-
Zr, Cr, Mn, Fe, Co, Rh, Ir	CO	-

hydrogen evolution. By using Sn, HCOOH was formed at higher current densities, i.e., under kinetically favourable conditions.

- On Zn, Pb and Cd cathodes, formic acid was formed at low or medium current efficiency. In 1985, Begotski *et al.*[110] confirmed the Ito's original results for the electroreduction of CO_2 on sp group metals.
- In 1987, Ito *et al.*[113] studied the product distribution as a function of cathode potential at various cathode materials such as In, Pb, Zn and Sn. It was confirmed again that, In electrodes are suitable for HCOOH preparation (rf = 87.6%). In and Pb in aqueous tetramethylammonium phosphate (TEAP), the best yields for HCOOH was obtained. When Sn and Zn cathodes were employed in aqueous TEAP solution, the rf ranged from 37 to 70% (Sn is a typical sp group [114,116] (4th group) metal while Zn, a transition element with d^{10} electronic configuration).
- Komatsu *et al.*[141] obtained HCOOH with good rf and ~ 10 mA/ cm^2 on Bi and Bi-plated GC electrodes. Sb was not effective for CO_2 electroreduction.
- The introduction of Cu and Cu- coated metallic electrodes for the preparation of hydrocarbons and/ or alcohol[123,142-149,150-158] in aqueous media is a real break through. It is to be emphasized that these reductions were performed at ambient temperatures and pressure at high current density, when neutral supporting electrolytes were used; the rf was of quantitative order[159,165]. Limitation of the electrodes lies in their quick deactivation (within 20-30 min. of electrolysis)[155]. A periodic anodic activation procedure allowed high hydrocarbon yields over prolonged electrolysis. The conclusion was further confirmed by Cook *et al.*[159] that the electrocatalytic activity of Cu depended on renewal of the electrode surface. Clean Cu surface allowed the achievement of rf values of 73% for CH_4 and 25% for C_2H_4.
- Katoh *et al.*[166] in 1994 studied the effect of microcrystalline structures of Cu-Sn and Cu-Zn alloys on the electrocatalysis of CO_2 reduction in 0.05 M $KHCO_3$ aqueous solution at low temperature 275 K. It was found that the selectivity, reversibility and reactivity for CO or HCOOH production strongly dependent on microcrystalline phase rather than the gross composition of alloys. The crystallites of the intermetallic compounds of $Cu_{5.6}$ Sn and Cu_5 Zn_8 were effective phases for the selective formation of CO with a high reaction rate.
- Hara *et al.*[167] in 1994 found that the selectivity of electroreduction products of CO_2 on Cu electrode in aqueous $KHCO_3$ solution depended on CO_2 pressure (< 60 atm), stirring conditions and the current density. It is concluded that the balance between the flux of CO_2 from the bulk solution to the electrode surface and the current density determines the product selectivity.
- Li and Prentice[168] in 1997, synthesized MeOH (rf = 40%) via the electroreduction of CO_2 in aqueous high pressure LiCl electrolyte at Cu electrode, at a current density of 9 mA/cm^2 at -1.1 V Ag/AgCl. Electrolyte conductivity in this system increased with temperature, increasing concentration of LiCl and decreasing pressure.
- Rotating disc electrodes were employed to ensure a constant transport to and from the Cu surface, since the products of electroreduction is continuously swept away from the surface of the disc[156]. However, the mechanism of CO_2 electroreduction on Cu is not still completely understood. No sufficient explanations were found for the behaviour of the supported Cu electrodes and for the influence of Cu^+ ions present in the supporting electrolyte[149,156-168].
- Hwang *et al.*[149] evaluated the experimental factors influencing the rf of Cu/GC cathodes for CH_4 and C_2H_4 formation. Maximum rf. obtained was 70% at pH 7 in aqueous solutions at room temperatures and at pH 2 at 273 K. The surface area of the electrode played a significant role toward the electrocatalytic reduction of CO_2. The presence of Cu-complexing agents in supporting electrolyte, such as ammonia, ethylenediamine or pyridine enhanced the efficiency of the electroreduction.
- Ikeda *et al.*[171] employed Cu-loaded gas diffusion electrodes for the mass reduction of CO_2. The products were found to be CH_4, C_2H_4, C_2H_5OH, CO and HCOO, but the current densities achieved for gas-diffusion electrodes were higher for two orders of magnitude than that for Cu plate electrodes.
- Kaneco *et al.*[169] in 1999, investigated the electroreduction of CO_2 with a Cu electrode in CsOH/methanol - based electrolyte. The main products formed were CH_4, C_2H_4, C_2H_6, CO and HCOOH. A maximum faradic efficiency of

ethylene was 32.3% at –3.4V/Ag-AgCl. The best methane formation efficiency was 8.3% at –4.0 V. The ethylene/methane current efficiency ratio was in the range 2.9 - 7.9. In CsOH methanol, the efficiency of H_2 formation, being a competitive reaction against CO_2 reduction was depressed to below 23%.

- Later, Kaneco *et al.*[170] studied the electroreduction of CO_2 with a Cu electrode in LiOH/methanol - based electrolyte. A divided H-type cell was employed; the supporting electrolyte was 8 mM LiOH in MeOH (catholyte) and 300 mM KOH in MeOH (anolyte). The main products were CH_4, C_2H_4, CO and HCOOH. In LiOH/MeOH, the H_2 formation was depressed to be low 2% at relatively negative potentials. The highest rf values for CO and hydrocarbons were achieved with electrodes made up of pure and small particle size Cu powder[171].
- Komatzu[172a] employed composite cathodes made up of Cu-deposited on to a solid polymer electrolyte. When Cu on a cation-exchange membrane (Nafion® 117) was used C_2H_4 was the main product, while Cu on an anion-exchange (Selemion AMV, styrene-divinyl benzene copolymer type) membrane was selective for HCOOH.
- Solid polymer electrolyte (spe) method can be applied to the electrochemical reduction of CO_2 in the gas phase, without solvent, because no supporting electrolyte is required. This method thus provide the absence of the catalyst poisoning owing to solvent or electrolyte impurities and an increased mass transfer over that in solution. Gas-phase electrochemical reduction of CO_2 using Cu-spe composite electrodes has been already investigated by Dewulf and Bard[172b] and Cook *et al.*[172c]. Work by Dewulf and Bard showed that the Cu/Nafion electrode can be prepared by using a N_2H_4 reducing solution and a Cu (II) - pyrophosphate plating solution, but it took a very long time ~2 weeks for electroreduction. Cook *et al.,* carried out the deposition of Cu on Nafion membrane by the combination of $CuSO_4$ and $NaBH_4$, but the technique was not clearly described. Komatsu *et al.*[172a] in 1995 fabricated Cu-Nafion electrode by an electroless plating method by combination of Cu - Rochelle salt as the plating agent and 10% $NaBH_4$ as the reducing agent. With the electrodes made of cation-exchange (Nafion) and anion exchange (Selemion) membrane as spe materials, the total current efficiencies for reduction product of CO_2 had maximum values of 19 and 27% respectively. The use of the former gave C_2H_4 as the major product while the latter, HCOOH and CO were obtained.
- Although similar in their electronic configuration and alike in most of their chemical properties, Cu and Ag behaved differently, when employed as cathode in CO_2 electroreduction. Watanabe *et al.*[173] employed *ab-initio* MP_4 calculation, to explain the difference. Their calculations suggested that CO did not interact with Ag, but that it was adsorbed on the Cu electrode, the C-O bond being weakened in the latter case. The optimized geometry and vibrational wave numbers of Cu CO^- were determined, but there was no evidence for the existence of Ag CO^-.
- Pressurized conditions leads to improved rf for electroreduction of CO_2. For instance, for principal group cathodes at 30 atm, formic acid was obtained with excellent faradic yields[174]: 95.5% on Pb, 92.3% on Sn, 90.1% on In and 82.7% on Bi. Despite the similarity of In and Al, the latter metal scarcely exhibits catalytic activity for CO_2 reduction, only H_2 was produced exclusively (86.5%). High pressure GC and n-Si wafer cathode reduced CO_2 efficiently to CO and HCOOH to 46.3% HCOOH respectively. It was felt necessary to activate the GC electrode by applying a 30s anodic pulse at +1.2V/SCE[175].

  The mechanism of CO_2 electroreduction on sp group metal electrodes is schematically represented in Fig. 9.

2.6.1.2 Role of Supporting Electrolyte

It is generally known from the number of investigations that the current efficiency of CO_2 electroreduction depended on the nature of the cation and anion present in the supporting electrolyte. It was found that the presence of CO_3^{2-} or SO_4^{2-} anions in the solution increased the rf, while PO_4^{3-} did not enhance the Faradic yield[176,113,119,122]. The rf improvement by CO_3^{2-} and HCO_3^- was attributed to their direct participation in the mechanism of CO_2 electroreduction. Therefore, the actual mechanism of CO_2 electroreduction appears to be more complicated than that initially assumed.

Ulmann *et al.*[121,122] attributed the high cathodic currents observed in aqueous $CsHCO_3$ solution to the participation of HCO_3^- ions in the mechanism of

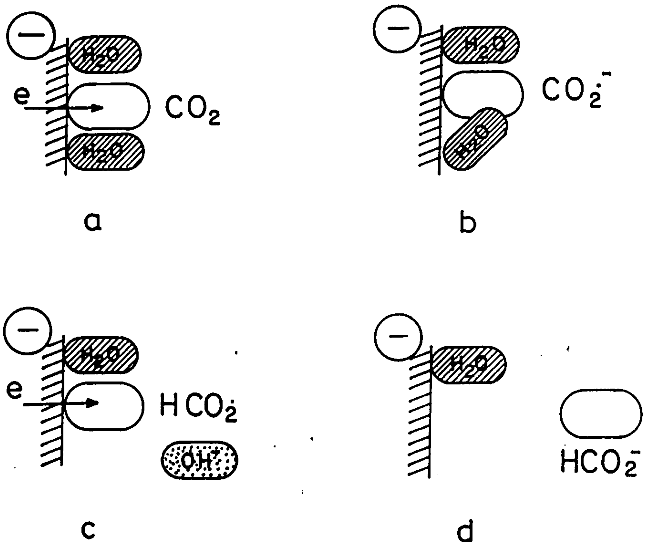


Fig. 9 Mechanism of CO_2 electroreduction on sp group metal electrodes. Neutral hydrated CO_2 molecules (a) undergo electronation to yield qadsorbed CO_2^-radicals; (b) the latter react with adsorbed water molecules to form adsorbed HCO_2 radicals and OH^- ions; (c) HCO_2^- radicals remain adsorbed at the electrode surface and undergo further reduction to formate ions; (d) the negatively charged $HCOO^-$ ions are rejected from the electrode surface

electroreduction of CO_2. Alternate perception is that it is HCO_3^- ions, which undergo electroreduction rather than the neutral CO_2 molecules. The rf values for HCOOH formation for various anions present in the supporting electrolyte found to increase from 35 to 57.5% in the order: $PO_4^{3-} < SO_4^{2-} < CO_3^{2-} < HCO_3^-$. These data can be explained by taking into consideration, the electrosorption of the hydrated ions at the electrode surface. This explanation was already proposed for other electroreduction processes[108,109,177-182].

Hori *et al.*, [101] in 1988, investigated the influence of various aqueous supporting electrolytes such as KCl, $KClO_4$, K_2SO_4 and K_2HPO_4 towards the electroreduction of CO_2 at Cu electrode at ambient temperatures and pressures. The products were found to be C_2H_4 (rf = 48%) and EtOH and n-PrOH in appreciable amounts. It was found that faradic efficiency of the products depends on the nature of supporting electrolyte.

Todoroki et al.[183] in 1995, studied the electroreduction of CO_2 under high pressure in aqueous $KHCO_3$ solution at metal electrodes with high overpotentials for hydrogen evolution such as Pb, Hg and In. When the electrolysis was conducted under high pressure CO and HCOOH was formed with rf = 100% even at high current density ~200 mA/cm^2 . The maximum partial current density of HCOOH formation amounted to 560 mA/cm^2 at the In electrodes at 60 atm of CO_2. On the other hand, CO was the main product at Pb and In less than 1 atm of CO_2. It was found that the selectivity of product formation depends on electrode potential. The less negative were the potentials, the higher the faradic efficiency for CO formation.

Small cations, such as Li^+ and Na^+ are not adsorbed at the electrode surface, due to their strong hydration. Further, small cations carry to the cathode a large number of water molecules, and thus supply protons for the electroreduction[178]. In contrast, the less hydrated bulky cations preferentially adsorbed at the cathode. Depending upon the nature of cation present in the supporting electrolyte the current efficiency of the process increased from 47 to 90% in the order: $Rb^+ < K^+ < Na^+ < Li^+$. Kyriacou and Anagnostipaulos[184] reported that rf for ethylene increased with the cation in the order $Cs^+ \sim K^+ > Li^+$. The non-metallic NH_4^+ cation allowed only hydrogen evolution to the extent of rf = 92%. This behaviour was attributed to the radius of the cation.

Potentiostatic CO_2 reduction studies carried out by Ito[112,113,185] and Komatu[141] in neutral $KHCO_3$ solution showed that: (i) Hg, In, Sn, Pb and Bi favoured the formation of HCOOH and $HCOO^-$; (ii) Zn and Cd, both with d^{10} electronic configuration (ie, sp group metals) exhibited poor electrocatalytic properties in the synthesis of HCOOH (eg: on Zn 20% $HCOO^-$ and 40% H_2; on Cd 39% $HCOO^-$ and 37% H_2), (iii) the main product on Ag and Au was CO. (iv) All other metals produced only hydrogen; (v) the favourable properties of In, suggested the opportunity of testing the electrocatalytic activity of 3rd group metals.

Azuma *et al.*[186] studied the electrochemical CO_2 reduction on 32 metal electrodes in aqueous $KHCO_3$ medium. The current efficiency of CO_2 reduction on Ni, Ag, Pb and Pd found to increase significantly with lowering the temperature. Lowering temperature also changed the ratios of reduction product. Potential dependence of HCOOH and H_2 on Hg electrode supports the electron transfer mechanism for HCOOH production. Formation of methane and ethylene is observed on almost all metal electrodes employed, though the efficiency is low except for Cu. A periodic table for CO_2 reduction Fig. 10 was drawn based on the dependence of reduction products on various metals, suggesting the existence of a systematic rule

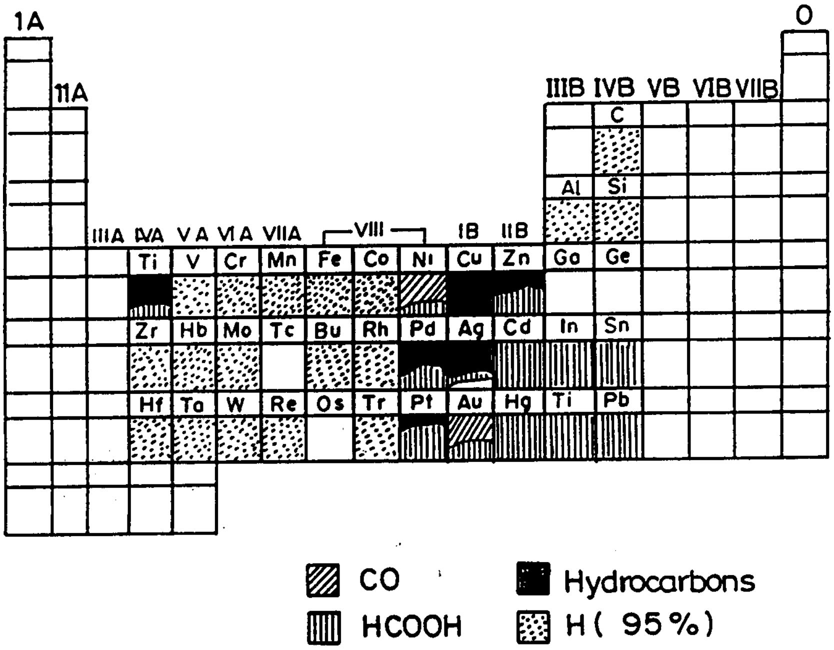


Fig. 10 Periodic table for CO_2 reduction products at –2.2 V /SCE in low temperature, 0.05 M $KHCO_3$ solution

for the electrocatalytic reduction of CO_2 on metal surfaces. Hori *et al.*[187] studied the electrochemical reduction of CO_2 in 0.5 M aqueous $KHCO_3$ solution at a gold electrode at 291K, the reaction proceeding with very low overvoltage, starting at -0.8 V/NHE; The product was found to be CO (rf = 91%) at -1.10 V/NHE, with partial current density of 3.7 mA/cm^2.

Eggins *et al.*[188] studied the electroduction of CO_2 on various metallic cathodes in the presence of aqueous quaternary ammonium salt as the electrolyte. On Hg and graphite, oxalate ions formed, on Pb glyoxylic acid was observed, while on Hg, malic acid was obtained. Similar reports were obtained by Bewick[189,190], Wolf and Rollin[191] and Kuhn[192]. The formation glyoxylic acid among the reaction products was in agreement with the previously known reduction of oxalate to glyoxalate on Pb cathodes[193]. The reaction mechanism is presented in the previous section of this article.

The electroreduction of CO_2 at graphite electrode at -0.9V/SCE in the presence of aqueous NH_4Cl as supporting electrolyte, yielded oxalate ions (rf = 78%), but the nature of the products varied as a function of cathode potential[188-192]. Ayres found the formation of MeOH with rf=100%, at graphite electrodes, at the same cathode potential of -0.94V/SCE, but the current density was maintained at low values (33-100 μA/cm^2)[194]. In the presence of Pb cathodes in aqueous NH_4Cl, good oxalate yields were obtained at -1.26 V/SCE.

Ito *et al.*[111,112], obtained CO, H_2 and $HCOO^-$ on gold, for electroreduction of CO_2. The nature of the product was determined by the cathodic polarization; for instance, from -1.3 to -1.6V/SCE exclusively CO and H_2 were formed[142-144]. Hori *et al.,* obtained a mixture of $HCOO^-$, CO, CH_3OH, CH_4 and C_2H_4.

When Ag was polarized to -0.8 V/SCE, MeOH was obtained with the Faradaic yield, rf ≤ 78%, but at very low current densities of 11 μA/cm^2 [195]. At cathode potentials more negative than -1.4V/SCE, exclusively CO was formed[195]. The presence of CO, ethane and methane among the reaction products was also confirmed by Noda[127]. The magnitude of the products yields was decided by cathode potential, as follows:

	$HCOO^-$	CO	C_2H_4	CH_4	C_2H_5OH
E(V,Ag/AgCl) =	-1.4	-1.52	-1.58	-1.70	-1.65

Kostecki and Auguestynki[196] found the poisoning of a polycrystalline Ag cathode during the electroreduction of CO_2 to CO. As for the Cu cathodes, a periodic anodic stripping of the Ag surface was efficient in removing the inhibiting species, and producing stable current densities and rf of CO formation over 4-5h of electrolysis run.

Shiratsuchi *et al.*[197] in 1996 have achieved a large degree of selectivity of reduction products of CO_2 on Ag electrodes by a pulsed technique. The anodic (Va) and cathodic (Vc) bias was found to be key parameters. The maximum faradic efficiencies for CO, CH_4, C_2H_4 and C_2H_5OH were respectively 70% (Vc

= -2.0 V, Va = -0.125V), 55% (-2.25V, - 0.4V), 3.1% (-2.25V, -0.4V), 3.1% (-2.25V, -0.4V) and 22% (-2.25V, -0.5V). The total value of 58.1% for CH_4 and C_2H_4 formation recorded on the Ag electrode is comparable with that for CH_4 and C_2H_4 formation on the Cu electrode which has long been considered as a unique metal for CH_4 and C_2H_4 formation. In addition, in the potential range where CH_4 and C_2H_4 are preferentially produced, the formation of HCOOH was found to be almost zero. The selectivity was ascribed to be due to the extent of the surface coverage of adsorbed H_2, which can be controlled by the anodic bias.

Kaneco *et al.*[198] investigated the electrochemical reduction of CO_2 in 0.1 M KOH-methanol electrolyte with an Ag electrode at 248, 258 and 273 K. The main products from CO_2 were CO and HCOOH. A predominant formation of CO from CO_2 on Ag electrode in the methanol electrolyte was found. The formation efficiency of CO increased at relatively negative potential as temperature decreased and in contrast, H_2 formation efficiency decreased. The reactivity of CO_2 reduction over H_2 evolution was ameliorated by lowering temperature. From the Tafel plot study, a sufficiently high mass transfer of CO_2 to the electrode was confirmed even in low temperature region consequently it was found that low temperature was extremely effective for the depression of H_2 formation on Ag electrode in KOH-methanol.

Yamamoto *et al.*[199] recently examined the electroreduction of CO_2 on high-area metal (Fe, Ni, Cu and Pd) electrocatalysts supported on activated carbon fibres, which contain slit-shaped pores with widths on the order of 2 nm. These catalysts exhibited relatively high selectivity (rf_{total} = 67%) and high partial current density (~63 $mAcm^{-2}$ on Ni). Much smaller activities were observed for the same types of metal catalysts supported on non-activated carbon fibres. The enhancement of CO_2 reduction selectivity with the micro porous support is thought to involve a nanospace effect, which give rise to high-pressure-like effects at ambient pressures. The CO_2 reduction mechanism on Ni is proposed to involve an absorbed CO_2-CO_2^-adduct, which is known to exist on (110) surface.

It is therefore concluded from these assimilated data that:

(1) On sp metal electrodes in aqueous supporting electrolytes the main product is formic acid.

(2) The catalytic activity of the cathode decreased in the following order.

In ≈ Bi > Hg > Pb > Sn > Zn ≈ Cu > Cd > Hg > Ag > Au > Sb

2.6.1.3 Electroreduction in Non-aqueous Media

The purpose for employing nonaqueous supporting electrolytes were: (i) To increase CO_2 solubility and to suppress H_2 evolution and thereby increasing current efficiency[194], (ii) The occurrence of dimerization process, leading to the formation of higher value C_2 products. As already mentioned, CO_2 has better solubility in organic-solvents than in water, irrespective of dielectric constant of the solvent.

- Chang *et al.*[199] found that elevated pressure of CO_2 showed a highest solubility order in cyclohexane, intermediate solubility in toluene and lowest solubility in DMF.
- CO_2 electroreductions performed on Pb, Tl and Hg electrodes in non-aqueous media yielded oxalate ions. On other sp group metals (ln, Zn, Sn and Au), a reductive disproportionation of CO_2 occurred with the formation of CO and carbonate ions. This process was first recognized by Savent *et al.*[200,201].
- Chronoamperometric reductions on Au and Hg electrodes in anhydrous DMSO yielded CO molecules[202]. The standard reduction rate constants were significantly lower for Hg (3.2 x 10^{-25} cm/S) than for Au (4 x 10^{-12} cm/S). No evidence for the role of solvent in redox process and no reasonable explanation were provided for the very low rate constant at Hg electrodes.

  Gennaro *et al.*[203] in 1996, found that there is a striking difference between direct electrolysis of CO_2 in DMF at an inert electrode such as Hg, which produces mixtures of CO and oxalate and electrolysis catalyzed by radical anion of aromatic esters and nitriles produces exclusively oxalate in the same medium. Examination of previous results concerning direct electrochemical reduction and reduction by photo injected electrons reveals that there is no significant specific interactions between reactants, intermediates and products on the one hand and the electrode material on the other. Later, same authors proposed a mechanism for this process[203b].
- Vassiliev *et al.*[204] investigated the electroreduction of CO_2 on Sn, In, Pb and Hg in various non-aqueous solvents such as DMF, DMSO and acetonitrile. The main reaction was found to be dimerization, leading to the formation of oxalate ions.
- Ito *et al.*[129] carried out the electroreduction of CO_2 in an electrolyte consisting of TEAP, a quaternary

ammonium salt in DMSO or propylene carbonate (PC). Oxalic acid was the principal product (rf ≤ 80%) on lead electrodes, while CO was the sole product on Sn and In cathodes. Under similar conditions, a mixture of oxalic acid, glyoxalic acid and CO was obtained when Zn electrodes were used, with overall rf of ~ 40%. The same authors[107] extended their studies to Pb, Tl and Hg electrodes under similar conditions in TEAP/PC and oxalic acid (rf ≤ 84%) was selectively formed. Pb cathode in TEAP/PC, the concentration of oxalic acid increased linearly with temperature, up to 423 K[107]. Above this temperature limit, glyoxylic acid, glycolic acid started to form. Glyoxylic acid was also obtained on Cd[107], but the main reduction product was CO.

- On sp group metals, in addition to oxalic and glycolic and formic acids, several other carboxylic acids were obtained during CO_2 electroreduction[205]: eg. Tartaric acid on Pb and Zn; malonic acid on In, Zn, Sn and Pb, propionic acid on Zn, Sn and Pb and n-butyric acid on In. Sn and Pb. The best non-aqueous reductions occur on Pb and Sn, with rf $\simeq$ 50% on Pb cathode. But current efficiencies are very low in the order of ≤ 10 mA/cm^2 [206].
- CO_2 electroreduction was performed on a Cu cathode in a benzalkonium chloride/methanol-supporting electrolyte, at low temperature[145,146]. At 258 K, CO (24.0%), CH_4 (39.1%) and C_2H_4 (4.4%) [145] were formed. The rf of both CH_4 and C_2H_4 was better in pure MeOH than in aqueous-electrolytes. The solubility of CO_2 in MeOH is about five times that in water at ambient temperature.
- Mizuno *et al.*[207] in 1995, improved this method by cooling the same supporting electrolyte even to a lower temperature of 243K. The rf of CH_4 exceeded 42%. In addition, the efficiency of the competing hydrogen evolution was diminished to less than 80% at low temperatures.
- Methanol is a solvent, which allows the electroreduction of highly concentrated CO_2 solutions[208]. The mole fraction of CO_2 is 0.34 at 4.0 MPa, and 0.94 at 5.8 Mpa[209]. In such highly concentrated solutions the supply of CO_2 to the electrode is more for the reduction to proceed at high current density. The main products of this electroreduction in the presence of tetrabutylammonium (a hydrophobic environment) were, CO (rf≤48.1%), CH_4 (rf ≤ 40.7%), C_2H_4 (rf ≤ 9%) and $HCOOCH_3$ (rf ≤ 34.6%). In contrast, Li salt supporting electrolytes (a hydrophilic environment) enhanced the formation of methyl formate[209]. The mechanism was as follows:

  $CO_2^{-\bullet} + 2H^+ + e^- \rightarrow HCOOH$ ...(35)

  $HCOOH + CH_3OH \Leftrightarrow HCOOCH_3 + H_2O$ ...(36)
- When the high current density electroreduction on a Cu cathode was conducted at elevated pressure[209]; the mass transfer of CO_2 no longer limited the formation of CO. At 40 atm and -2.3 V/Ag, quasi-reference electrode, the total current density was 436 mA/cm^2, while the rf of CO_2 reduction reached 87%. In the gas phase, CO, CH_4, C_2H_4 and H_2 were found as products, while the main products in liquid phases were methyl formate and dimethoxymethane (CH_3O-CH_2-OCH_3)[209]. Methanol is at the present time, employed in industry as a CO_2 absorber. The systems above may find their industrial applications in large-scale methane production.

To conclude, on the sp group metal cathodes in aqueous supporting electrolytes, the main product was formic acid in neutral solution and formate ions in alkaline solution, while in non-aqueous media oxalate ions were the predominate product[206].

2.6.2 Electroreduction of CO_2 on 'd' Group Metals

2.6.2.1 In Aqueous Media

(A) Pt, Pd and Ni Electrodes

Platinum group metals generally exhibit favourable electrocatalytic properties for the electroredution of CO_2 due to the strong adsorption of CO_2 on these metals. The nature of product formed on Pt, Pd and Ni was controlled by the experimental conditions[210-243].

Pt cathodes

- Cyclic voltammetric studies performed at Pt cathodes showed three intermediates generated from the adsorbed CO_2 [244]. Maier *et al.*[219] investigated the influence of temperature and prepolarization on the adsorption of CO_2 at Pt electrodes. At high temperatures, followed by anodic polarization at +0.520 V/SCE, formation of COOH species was found. Subsequent prepolarization at more positive electrode potential + 0.650 V/SCE, for 0.5h, the adsorbed species was mainly $(CO)_{ads}$. The oxidation peak at + 0.280 V/SCE found in CV was assigned to the formation of adsorbed $(HCOOH)_{ads}$.
- The surface of the electrode material plays an important role in product selectivity optimization

and in better current efficiencies. It was shown that the atomic arrangement of the Pt electrode surface significantly affects the rate of CO_2 reduction. Numbers of fundamental studies were carried out for the electroreduction of CO_2 on the three basal planes of Pt: Pt (100), Pt (110) and Pt (111)[222-226,245,246]. In acidic solution the most active site phase was Pt (110), which generated CO, while Pt (111) surface was inactive. The amount of reduced CO_2 increased when defects were present at the surface; these defects blocked preferentially the (100) terraces, whereas the edge sites were less active for the adsorption. The formation of CO at the Pt (110) surface was the result of the reduction of either HCO_3^- ions or of neutral CO_2 molecules produced by the dissociation of hydrogen carbonate ($CHCO_3^- \leftrightarrow CO_2 + OH^-$)[224,225,246].

Hara *et al.*[247] in 1995, investigated the effects of current density, CO_2 pressure and charge passed on the gas phase CO_2 reduction under high pressure (< 50 atm) on a gas diffusion electrode containing Pt electrocatalysts. The rf for CO_2 reduction reached 46% at a current density of 900 mA/cm^2; CH_4 (rf = 35%), a partial current density of 313 mA/cm^2; C_2H_5OH of (rf = 2.2%) and current density of 19.8 mA/cm^2.

The use of single crystal surface plays a key role in identifying the surface structure that gives high catalytic activity and selectivity in chemical reactions in gas / solid and liquid / solid interfaces. Studies using single crystals give useful information for the development of catalysts on which reactions proceed with low activation energy and high selectivity. Nikolic *et al.*[224a] first demonstrated that the reactivity of CO_2 reduction on Pt electrodes depends on the crystal orientation. Hoshi *et al.*[224b] measured the rates of CO_2 reduction on stepped surfaces of Pt such as Pt(s)-[n(111) x (111)]; Pt(s)-[n(111) x (100)] and Pt(s)-[n(100) x (111)][224c]. The reduction rates become higher with the increase of step density in each series comparing the rates among the surfaces with the same step density gives the following order of the activity for CO_2.

Pt(111) < Pt (100) < Pt(s)-[n(111) × (100)]
< Pt(s)-[n(100) × (111)] < Pt(s)-[n(111) × (111)]
< Pt (100).

The Pt(110) has the highest activity among the 'stepped' surfaces. Later[224d], they have extended their study to the 'kinked' step surfaces, such as Pt(s)-[n(110) x (100)] and Pt(s)-[n(100) x (110)], in order to find out which surface have a reduction rate of CO_2 higher than that of Pt(110). It was found that high activity in CO_2 reduction was derived from the kink sites characteristic of Pt(s)-[n(110) × (100)] and Pt(s)-[n(100) × (110)].

Even, well-ordered Pt (111) single crystal electrodes become active for CO_2 adsorption by activation in the Pt oxide potential region[226]. This treatment caused disorder at the surface, and thereby increasing the electrocatalytic activity of the electrode. Species proposed for the reduced CO_2 on polycrystalline Pt include: linear - CO_{ads} [248], bridged > CO_{ads} [249], -COOH [250-254] and ≡ COH [254,255] FTIR studies revealed the presence of both linear -CO (2030-2020cm^{-1}) and traces of bridge-bonded CO (1850, 1750 cm^{-1}), formed on a polycrystalline Pt surface[224,224,245].

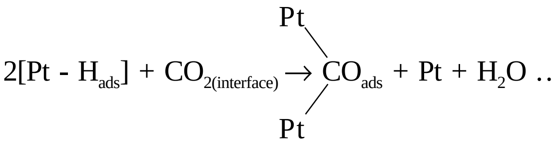
Hoshi and Hori[224e] carried out electrochemical reduction of CO_2 at a series of Pt single crystal electrodes and arrived into the following conclusions: (i) Flat surfaces; Pt (111) and Pt (100), have low activity for CO_2 reduction, (ii) The initial rate of the CO_2 reduction gets higher with the increase of the step atom density, (iii) the terrace and step structures affect the potential dependence of the initial rates remarkably, (iv) The activity for CO_2 reduction depends remarkably on the symmetry of the surface. As shown in their previous study[224b,224c], the Pt (110) has the highest activity for CO_2 reduction in the stepped surfaces, (v) Kinked step surface have higher activity for CO_2 reduction than stepped surfaces, (vi) Pt(s)-[n (100) x (110)] series, which have densely packed kink atoms along step lines, have the highest activity for CO_2 reduction.

Taguchi and Aramata[246] suggested a three-step mechanism for the formation of adsorbed linear CO [equations (37), (38), (39a)] and adsorbed bent CO [eqs. (37), (38), (39b)] respectively.

$$H^+ + e^- + Pt \rightarrow Pt - H_{ads} \qquad \ldots(37)$$

$$CO_{2(solution)} \rightarrow CO_{2(nterface)} \qquad \ldots(38)$$

$$2[Pt\text{-}H_{ads}] + CO_{2(interface)} \rightarrow Pt\text{-}CO_{2ads} + Pt + H_2O \qquad \ldots(39a)$$



$$2[Pt - H_{ads}] + CO_{2(interface)} \rightarrow \begin{matrix} Pt \\ \diagdown \\ CO_{ads} \\ \diagup \\ Pt \end{matrix} + Pt + H_2O \qquad \ldots(39b)$$

In CO_2-saturated aqueous solution, the Pt surface became covered with a strongly attached 'reduced CO_2' layer[127]. This adsorption layer hindered the further electroreduction of CO_2. Thus, the main process on Pt electrodes was hydrogen evolution.

Bandi *et al.*[244a] performed high-pressure electrolyses at Pt-cathodes in the presence of tetralkyl ammonium salts, both in aqueous-solutions and in supercritical CO_2. Walther *et al.*[244b] in 1999 discussed in detail on various aspects of compressed CO_2 and metal catalyzed reactions with CO_2 in which CO_2 as a reaction medium and as solvent and/or reagent.

Pd Cathodes

In bulk Pd cathodes[119,120] HCO_3^- was the electrochemically active species. Electroreduction of CO_2 to $HCOO^-$ with high current efficiencies was achieved on Pd cathodes. Ayers and Farley proposed a new approach for CO_2/HCO_3^- on flat bipolar Pd electrodes[216]. In this process, the atomic hydrogen penetrated the negative side of the bipolar Pd electrode. Once arrived at the opposite, positively polarized side of the electrode, hydrogen reduced the neutral CO_2 molecule, according the following sequential steps.

$$(HCO_3^-/CO_2)_{ads} + 2Pd - H \rightarrow HCOOH + 2Pd \quad \ldots(40)$$

$$(HCO_3^-/CO_2)_{ads} + 4Pd - H \rightarrow HCHO + H_2O + 4Pd \quad \ldots(41)$$

$$(HCO_3^-/CO_2)_{ads} + 6Pd - H \rightarrow CH_3OH + H_2O + 6Pd \quad \ldots(42)$$

CO_2 molecules adsorbed to the slightly positive face of Pd. No oxidation of the intermediates occurred.

Azuma[186] investigated the possibility of obtaining C_1-C_6 hydrocarbons, on bulk Pd electrodes but only low current efficiencies were realized. Ohkawa *et al.*[152,153] found an increase of rf of both CO and HCOOH following the adsorption of hydrogen onto the Pd electrode. The electrochemical hydrogen evolution was suppressed upon loading the electrode with molecular hydrogen from an external source. Adsorbed hydrogen may also react with the intermediates. The Tafel plots for CO_2 electroreduction on H-loaded Pd were compared with those recorded on H-free Pd electrodes[153]. The competing desorption of hydrogen was found to enhance the electroreduction of CO_2.

Hashimoto *et al.*[154] studied the electroreduction of CO_2 in aqueous $KHCO_3$ using the hydrogen accumulated in a Pd cathode and the products were found to be HCOOH and CO. When the electrode was formed from Cu and Pd, methane and methanol were obtained in addition to HCOOH. Later[154], they have employed a combination of Cu (sp group metal) and Pd, (d group metal). For Cu electrodes modified with Pd, the current efficiencies for the three products were larger than for Pd electrodes modified with Cu. The enhancement of the process efficiency was attributed to the amount of hydrogen adsorbed by the working electrode, rather than by the change in the lattice morphology or the oxidation state of copper.

Bocarsly *et al.*[227,228] employed Pt and Pd electrode at pH 5, in the presence of pyridinium ion as a homogenous catalyst for the efficient formation of MeOH, by electroreducing CO_2. The substrate reduction benefited from the hydrogen released from two sources: the electroreduction of H^+ and from the pyridinium ions. The rf = 30% and the electroreduction of CO_2 proceeded at low over potentials. New equipments were patented for the electrochemical reduction of CO_2 on metals[229-231].

Now a days, formic acid is prepared using Pd electrodes at potentials higher than the reversible hydrogen potential, with current efficiencies close to 100%[232,233]. Reaction was carried out at ambient pressure in alkaline aqueous-supporting electrolytes (pH 8-10). It was proposed that adsorbed hydrogen took part in the slow step of the HCO_3^- electroreduction.

Furuya *et al.*, in 1997[234,235] examined the reactivity and selectivity of CO_2 reduction at gas diffusion electrodes made of Ru, Pd and their alloy (Ru: Pd = 1). It was found that the current efficiency for the formation of formic acid at the gas diffusion electrodes with Ru-Pd catalyst was 90% at -1.1V/NHE, in which the current density was 80 mA/cm^2. CO was also formed at Ru-Pd catalysts.

Iwakura *et al.*, in 1998[235], studied the electrocatalytic reduction of CO_2 on palladized Pd sheet electrodes. It was found that formic acid as the main product and H_2 evolution as a by-product. The maximum current efficiency for HCOOH was 75% and it depended on the reaction time and current density for the palladization.

The adsorption of carbon dioxide on Pd-Pt alloy electrodes in acidic solution has been studied recently by Grden *et al.*[217]. The influence of both bulk and surface composition of the alloy on CO_2 adsorption was presented. The results suggested that only hydrogen interacting with platinum atoms was active in reaction with CO_2. At the same time these platinum atoms were found to be inactive in the hydrogen absorption/ desorption process. It was presumed that the latter reaction proceed only with participation of palladium atoms, unblocked by products of adsorption of CO_2.

Ni Cathodes

Hori *et al.*[143] stated that hydrogen evolution was predominant on Ni when the electrolytes were neutral or mildly acidic solutions. Frese[206] obtained some CO (rf = 9%) in addition to hydrogen. Koga *et al.*[236,237] found that 99-99% pure Ni in aqueous-supporting electrolytes produce hydrocarbons (CH_4, C_2H_4, C_2H_6) and ethanol. However, the simultaneous hydrogen evolution could not be avoided[236]. The reactive intermediate CO strongly adsorbed at the Ni surface and this adsorbed layer occupied most of the surface sites when hydrogen evolution usually evolved and thus inhibited the hydrogen gas formation. The presence of CO_{ads} was evidenced by FTIR spectroscopy[237]. Later, they obtained hydrocarbon and traces of ethanol on pure Ni in neutral phosphate buffer under Ar and CO_2 atmosphere[237]; rf for CH_4 = 3.7%, C_2H_4 = 0.1%, C_2H_6 = 0.7% and ethanol = 0.1%. The H_2O reduction started at -0.45 V/SHE in Ar atmosphere and anodic oxidation of the Ni was observed at -0.18 V/SCE.

Koga *et al.*[238] found the formation of CO_{ads} at Ni electrode, as the intermediate for the products formed such as CH_4, C_2H_4 and C_2H_6.

The concentration of CO_2 in water at 298 K is only 0.033 mol / dm^3. At elevated pressure of 60 atm, at room temperature this can be increased to 1.17 mol / dm^3 a value close to the liquefying pressure of ~70 atm. Electroreduction of CO_2 was studied at Ni electrode under pressurized conditions. Comparative mechanisms of high-pressure CO_2 electroreduction (**A**) and the electroreduction of CO_2 at atmospheric pressure (**B**) is shown in Fig. 11[239]. In case (Fig. 11A), the hydrogen atoms formed at the electrode surface by the reduction of water are consumed in the reaction with adsorbed CO_2 to form reduction products such as CO and HCOOH. In contrast, at 7 atm pressures, most of the adsorbed hydrogen is desorbed in the form of H_2. The ratio of adsorbed CO_2^- radicals vs. adsorbed hydrogen atoms increases with increasing pressure[239]. Ito *et al.*[241,242] studied the electroreduction of CO_2 at high pressure (60-50 atm) on Group VIII metal electrodes such as Fe, CO, Ni, Pd and Pt and the rf values were as high as 62%.

Kudo *et al.*[239] in 1993, investigated high-pressure CO_2 electroreduction on high purity Ni cathodes in aqueous $KHCO_3$ supporting electrolyte using 99.9% CO_2. The increase of CO_2 pressures favored the rf of CO_2 reduction and diminished the hydrogen evolution by water reduction. Best hydrocarbon yields were achieved at -1.6V/Ag/AgCl at 303 K. More negative cathodic polarization (below -1.9V/Ag/AgCl) enhanced the rf for both CO and HCOOH. The weight distribution of hydrocarbons agreed with the Schultz - Flory distribution, suggesting a formation mechanism similar to thermally catalyzed Fischer - Tropsch reaction. Mechanisms are proposed for the products formation.

Hori *et al.*[243] employed a novel SNIFTIRS (Substractively Normalized Interfacial Fourier Transform Infrared Spectroscopy), to provide evidence for adsorbed CO at the Ni cathodes. At pH 6-8, in a CO_2 - saturated phosphate buffer solution, adsorbed CO was present at Ni - electrode surface in the potential range from -0.4 to 0.8V/NHE. Both linear and bridged CO molecules were detected. The linear CO appears at -0.8V/ NHE, since the reduction of adsorbed CO proceeded at cathode potential less than -1.0V/NHE. The bridged CO was presumed to be the electroactive species[107,143,161,256-261]. Ni cathodes possess the favourable electrocatalytic properties for the C_1-C_4 (CH_4, C_2H_6, C_3H_8, n-and i-butane) compounds formation. In contrast, Cu electrode is selective for the formation of CH_4 and C_2H_4.

(B) Fe, Ru, Os electrodes

Iron cathodes have been widely employed for CO_2 electroreduction. Hori *et al.*[143] found that Fe cathodes in neutral and mild acidic solutions yield predominantly hydrogen. Frese and Canfield[206] observed significant

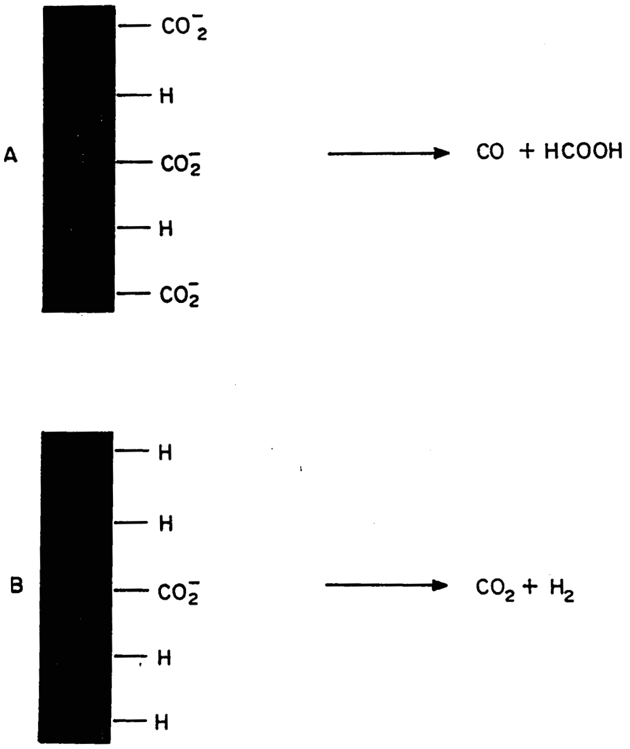


Fig. 11 Comparative mechanism of high-pressure CO_2 electroreduction (A) and the electroreduction of CO_2 at atmospheric pressure (B) on Ni cathode

amounts of CO on Fe cathodes. Hara *et al.*[174] in 1995, under high-pressure conditions (30 atm) at Fe cathode studied the electroreduction CO_2 and HCOOH was found to be the main product, methane as the side product and traces of ethane and ethylene were also found. The faradic yield was very low, about half of the current was consumed on hydrogen evolution. Latter, Hara *et al.*[262] under high-pressure conditions and at large current density (120 mA/cm^2) achieved 60% efficiency for HCOOH formation. By products were long-chain hydrocarbons such as 1-butene, trans-2-butene, iso-and n-pentanes, with a maximum partial current density of ~ 10 mA/cm^2.

Ruthenium was the first metal found to catalyze the electrochemical methation of CO_2 [211-213]. Chao *et al.*[214] employed Ru electrodes for electroreduction of CO_2 for the formation of MeOH (rf = 25%) and CH_4 (rf = 30%). Ru is one of the metals with an intermediate hydrogen evolution overpotential, which absorbs a considerable amount of hydrogen at under potentials. Therefore, one can expect that the reduction CO_2 will take place at this electrode at relatively small overpotentials, at which the hydrogen evolution will not be excessive. This will diminish the loss due to concurrent hydrogen evolution. The stability of the electrode surface under vigorous hydrogen evolution enables investigation of the kinetics of CO_2 reduction under long-term potentiostatic conditions. Reduction of CO_2 at Ru and Ru modified Cd and Cu ad atoms were investigated by Popi'c *et al.*[215] in aqueous 0.5 M $NaHCO_3$ solutions. Methanol and acetone were formed at the end of 8h electrolysis under the potential of -0.8 V/SCE. The process of methanol formation on Ru modified by the Cu ad atoms is catalyzed by the presence of ad atoms and the process of acetone formation is independent of the presence of ad atoms at Ru surface.

- Osmium cathodes at –0.69V/SCE and at low current density were selective for methanol formation (rf = 57%) and traces of CO (rf = 0.11%) were obtained. Carbon electrodes electroplated with osmium ceased the formation of methanol[206].

(C) Co, Rh and Ir Electrodes

Cobalt electrodes mainly yielded CO (rf <26%) in slightly acidic sodium sulphate or neutral lithium bicarbonate solution at 333 K[206]. Almost no reduction occurred on Rh and Co electrodes. When used at ambient pressure, the predominant product was H_2 from water reduction[174]. In contrast, at 30 atm pressure and elevated current densities (163-700 mA/cm^2); CO and HCOOH were obtained in addition to H_2. Under similar conditions, Rh electrode mainly yielded CO (61%) and HCOOH (19.5%). Ir electrodes decompose water to hydrogen (48.3%) and only limited quantities of formic acid (22.3%) and CO (17.5%) were obtained[174].

(D) Cr, Mo and W Electrodes

- Summers and Frese[263] employed Mo electrodes for the electroreduction of CO_2 to form methanol. In fact, Mo electrode is a metal/metal oxide system. When a CO_2 saturated sodium sulphate solution (pH = 4.2) was electrolyzed at –0.7 to –0.8V / SCE at room temperature, methanol was found as the main product, with rf = 50-100%. In dilute sulfuric acid, the methanol yields were in the range of 20 – 46%, CO (1-20%) and methane (0.1-3.0%)were the byproducts. Scanning the electrode potential from +0.2 V to –1.2 V/SCE enhanced the rate of methanol formation. A two-step reaction mechanism was proposed.

  $$2CO_2 + 3Mo + 4H_2O \rightarrow 2CH_3OH + 3MoO_2 \quad \ldots(43)$$

  $$3MoO_2 + 12H^+ + 12e^- \rightarrow 3Mo + 6H_2O \quad \ldots(44)$$
- CO_2 electroreductions at Mo cathodes in non-aqueous solvents such as PrC, DMSO and AN led to the formation of oxalic acid with current efficiencies in the range of 20- 35%, while 5- 30% of CO is formed as the byproduct[107].
- Tungsten electrodes operated at 33K in sodium sulfate solution at pH = 4 with low current densities of 32µA/cm^2, methanol was formed (rf = 76%) along with small amounts of CO (rf = 22%)[206]. Hara *et al.*[174] employed high-pressurized conditions to obtain 31.9%, oxalic acid and hydrogen was the byproduct with 53.1%.
- On chromium electrodes, hydrogen was the predominant product and CO was formed to a lesser extent (rf = 6.2%)[204]. At high-pressure conditions, (30 atm) CO (rf =11.8%) was formed along with HCOOH (8.2%)[174].

(E) Ti, Zr, Nb, Ta and Mn Electrodes

Under high-pressure conditions (30 atm) of CO_2, all four metals produced HCOOH to a smaller amount (3.5- 7.6%) with significant amounts of hydrogen. CO generation was notable in Zr(32.5%). At Mn electrodes operated at 30 atm, only 6.5% of CO_2 reduced to 2.8% of CO and 2.8% HCOOH with 78.8% of hydrogen formation[174].

2.6.2.2 'd' Group Metals in Non-aqueous Media

- Vassiliev *et al.*[204] studied the electroreduction of CO_2 at Pt in non-aqueous supporting electrolytes. The products were found to be CO and CO_3^{2-}.
- Ni and Pt electrodes in TEAP/Propylene carbonates electrolyte formed CO and HCOOH in the ratio from 6:1 to 8:1, wt/wt at -2-8V/Ag/AgCl. Trace amounts of oxalic acid were also formed[107]. In similar experiments performed on Pd electrodes, significant quantities of oxalic acid (CO/HOOC-COOH = 2:1, wt/wt) and trace amounts of formic acid were formed[107].
- Iron cathodes exhibit high selectivity for oxalic acid preparation.
- Ti, Nb and Cr electrodes in TBAP/propylene carbonate electrolyte formed oxalate, glyoxalate and glycolate anions. In Mo electrodes under similar conditions only oxalate was formed[107].

The main electroreduction products obtained on sp and d group metal cathodes in aqueous and non-aqueous supporting electrolytes are systematized in Table VII.

2.6 Reduction of CO_2 using Semiconductors

Since the reduction of CO_2 is an uphill process, it is desirable to carry out this reaction with a very low consumption of energy and/or with the use of a renewable energy source[264a]. The photo electrochemical reduction of CO_2 is hence an attractive pathway. Semiconductors have been used as cathodic materials, either in the dark or under light irradiation. Semiconductors occupy a special place in the electrochemical reduction of CO_2, due to the possibility of using them without an external source of electricity, either as photo electrodes with an external source of electricity, or as micro batteries suspended in solution. The charges necessary for the reduction process are generated by illumination. If the charges can be effectively separated, they can be involved in a number of electrochemical reactions. The separation is based on bending of bands of the semiconductor electrodes. The electron transfer from semiconductor electrodes towards CO_2 depends on the nature of the semiconductor.

In the course of the development of photo electrochemistry, a variety of p-type semiconductor electrodes such as p-CdTe, p-GaP[264b], p-GaAs, p-InP, p-Si, and p-SiC have been examined. Semiconductor electrodes whose surfaces are modified with metal particles are often known to exhibit improved photo electrochemical behaviour. p-Si electrodes modified with metal particles (Cu, Ag, or Au) were used by Hinogami *et al.* to reduce CO_2 in aqueous solution, resulting in the formation of CH_4, C_2H_2, CO, etc.[264c]. The reduction process was shifted in potential approximately 0.5 V positive compared to that obtained with the corresponding metal electrodes.

A high-pressure CO_2-methanol system has been found to offer a number of advantages for the photo electrochemical reduction of CO_2 by Hirota *et al.*[224d]. This reaction was examined in a 40-atm CO_2-methanol medium using the p-type semiconductor electrodes p-InP, p-GaAs, and p-Si. With p-InP photocathodes, current densities up to 200 mA/ cm^2 were achieved, with current efficiencies of over 90% for CO production, while hydrogen gas evolution was suppressed to low levels. At high current densities and CO_2 pressures, the CO_2 reduction current was limited principally by light intensity. Of the various factors that were found to influence the product distribution, including the concentrations of added water and strong acid, the CO_2 pressure was the most critical factor. It was proposed that the adsorbed $(CO_2)_2^{\cdot-}$ radical anion complex reaches high coverages at high CO_2 pressures and is responsible for both the high current efficiencies observed for CO production and the low values observed for H_2 evolution. In addition, this adsorbed complex is responsible for stabilizing all the three semiconductor electrode materials at high CO_2 pressures, even at current densities as high as 100 mA/ cm^2. Aulice Scibioh and Viswanathan[265] have recently reviewed the various aspects of photo/ photo electrochemical reduction of CO_2. Dispersed semiconductor particle suspensions are attractive, as each particle is made up essentially of a short-circuited photo anode and cathode. They find their utility in CO_2 reduction. However, the discussion on semiconductor-cathodes is not within the scope of the present discussion.

2.8 Electrocatalytic Reduction of CO_2

In general, the aim of the studies on electrocatalytic reduction of CO_2 is to find cathodes that discriminate the reduction of water to H_2 and favour the reduction of CO_2. A fundamental requirement is that the latter process occurs at a lower potential on such electrodes. The direct electrochemical reduction on most metallic electrodes requires higher negative potentials, up to -2.2 V/SCE and results in a variety of products, the distribution of which critically depends on the reaction conditions such as electrode materials, solvent systems and operation parameters including current density and CO_2 concentration. This has prompted the search for suitable catalytic systems capable of mediating the electroreduction. A most interesting approach of employing electrode or solution modifiers is that of homogeneous/heterogeneous catalysis. CO_2 is captured by a metal complex in solution and electrons are transferred to the carbon dioxide complex from an electrode with/without modification by a suitable catalyst. Molecular electrocatalysts are promising in many respects because of the selectivity and efficiency associated with homogenous/heterogeneous catalysis. In addition, subtle variations in the structure of the molecular relay can be introduced by an appropriate synthetic procedure (organic skeleton) or by a fine control of the transition metal centre environment (ligands).

From an experimental view point, the simplest way of associating an electrocatalyst, (whose function may be extremely complex but still can be regarded as 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 electrocalalyst 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. The principle of modified cathode is that, the molecular electrocatalyst particles are embedded in a polymer matrix containing an appropriate electron relay, the composites material obtained after deposition (or anchoring) onto a cathode surface act as an electrocatalyst. The general principles of both types are schematically represented in (Fig. 12a&b).

Transition metal complexes, which can reduce CO_2 electrocatalytically, to various products, are grouped into the following categories.

1. Phthalocyanine complexes
2. Porphyrin complexes
3. Metal complexes of 2,2’-bipyridine and related ligands
4. Phosphine complexes
5. Metal clusters and polymetallic complexes
6. Biphenanthroline hexaazacyclophane complexes
7. Azamacrocylic complexes
8. Macrocyclic ligands related to macromolecular functions

2.8.1 Phthalocyanine Complexes

Several metallophthalocyanines (MPCs) have been reported to be active towards electroceduction of CO_2 [266-269]. Modified electrodes have been employed for this purpose. In some cases, metallophthalocyanines deposited onto electrode surfaces have been used with aqueous solutions. Polymeric complexes either immobilized on carbon electrodes or incorporated in coated Nafion® membranes have also been employed. The mechanism of catalysis for these systems has not been well understood. Meshitsuka *et al.*[270] published the first paper regarding electrocatalytic reduction of CO_2 using nickel or cobalt PC in 1974. The catalyst

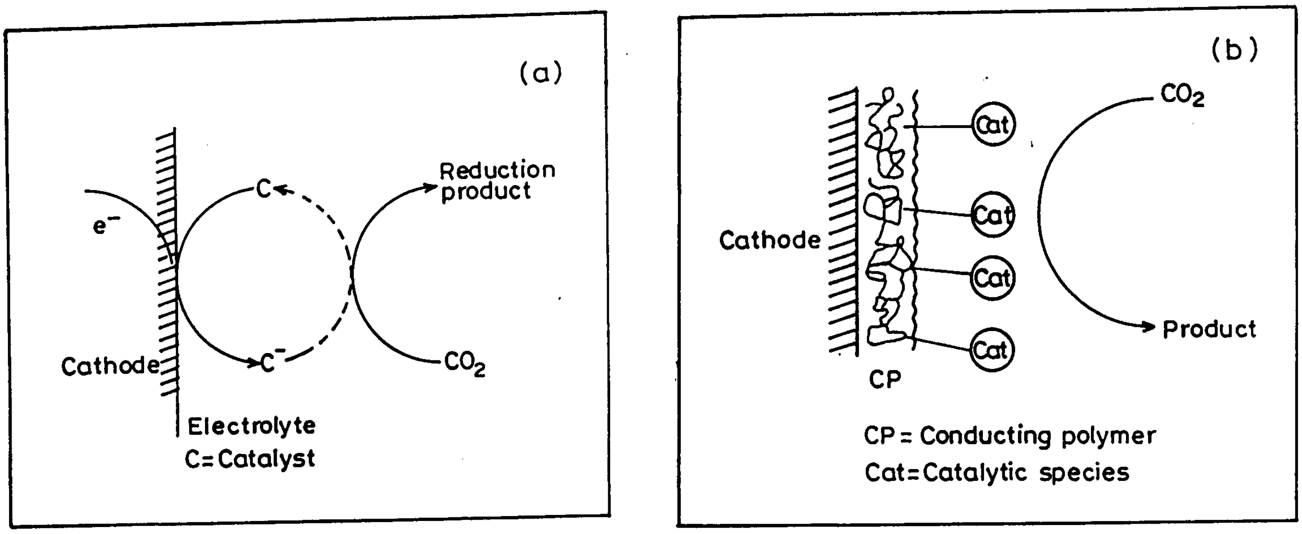


Fig. 12 (a) Molecular electrocatalysts in solution; (b) Cathodic materials modified by surface deposition of molecular electrocatalysts was deposited onto a graphite electrode by dip coating. The supporting electrolyte is a quaternary ammonium salt, the products were oxalic and glycolic acids but no formic acid was formed. These early experiments were not followed by accurate and detailed analytical work concerning the nature and quantities of reduction products. However, this system was slightly modified and re-examined 10 years later by American researchers[268,271]. Kapusta and Hackerman[268] showed that using CoPC as electrocatalyst, $HCOO^-$ was the main reduction product at pH > 5 (η=60%) in an aqueous electrolyte. At more acidic pH, methanol was also formed in small quantities (η=5% at pH 3). For the other metallophthalocyanines tested, the activity sequence is CoPC > NiPC >> Fe PC, CuPC > $CrPC^+$. Under experimental conditions very similar to those used by Kapusta and Hackerman, other authors[271] obtained mainly CO and H_2 in the 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 was not established which experimental factor was responsible for this dramatic difference between the products formed in the two studies discussed above.

CoPC has been reported to be one of the most active pthalocyanines for CO_2 reduction[267-270], and the mechanism of the reduction in aqueous solution is believed to involve cobalt hydride intermediates[271]. The results were interpreted in terms of the formation of a CO_2 adduct with the reduced phthalocyanine complex[272] as shown in Fig. 13.

When tin, lead and indium phthalocyanines are used, the main products are formic acid and H_2[273], while for copper, gallium and titanium phthalocyanines the main products are CO and hydrogen but methane is also produced with a good yield (about 30%)[273].

Iron, zinc and palladium phthalocyanines also give CO as the leading reduction product, but in lower yields compared with those obtained with cobalt and nickel phthalocyanines. Hydrogen is exclusively produced with magnesium, vanadium, manganese and platinum derivatives and with the free base[274]. These distributions of product (and current efficiencies) depend strongly on the chemical properties of metal and ligand[273], and suggest that the mechanism of CO_2 reduction is different for each group. The mechanism for producing a particular product may be determined by the interaction between the phthalocyanine ring, the central metal and CO_2 or CO molecules. The electrocatalytic reduction of CO_2 in an aqueous system using a modified graphite electrode coated with hydrophobic poly (4-vinylpyridine-co-styrene) (denoted PVP-st) containing CoPC has been studied by Abe *et al.*[276]. It was found that compared with CoPC-P (VP-st) system, the neat CoPC system gave high selectivity for CO_2 reduction[276]. It might be due to the fact the pyridine group of P (VP-st), which has both weekly basic and coordinative properties could have played a role. In their latter studies[277], they employed a modified graphite electrode coated with a poly (4-vinylpyridine) (PVP) membrane containing cobalt phthaloyanine (CoPC) for the electroreduction of CO_2. In 0.1 M NaH_2PO_4 aqueous phase (pH 4.4) the catalyst membrane exhibited a highest selectivity for CO_2 reduction than that by neat coating. (the ratio of CO/H_2 produced is 6 at -1.20 V/Ag-AgCl).

Abe *et al.* in 1996[277], investigated the electrocatalytic CO_2 reduction using a modified graphite electrode coated with cobaltoctabutoxyphthalocyanine (CoPC $(BuO)_8$) dipped in an aqueous electrolyte. CO was produced with higher activity and selectivity than in non-substituted CoPC. At pH 4.4, most selective

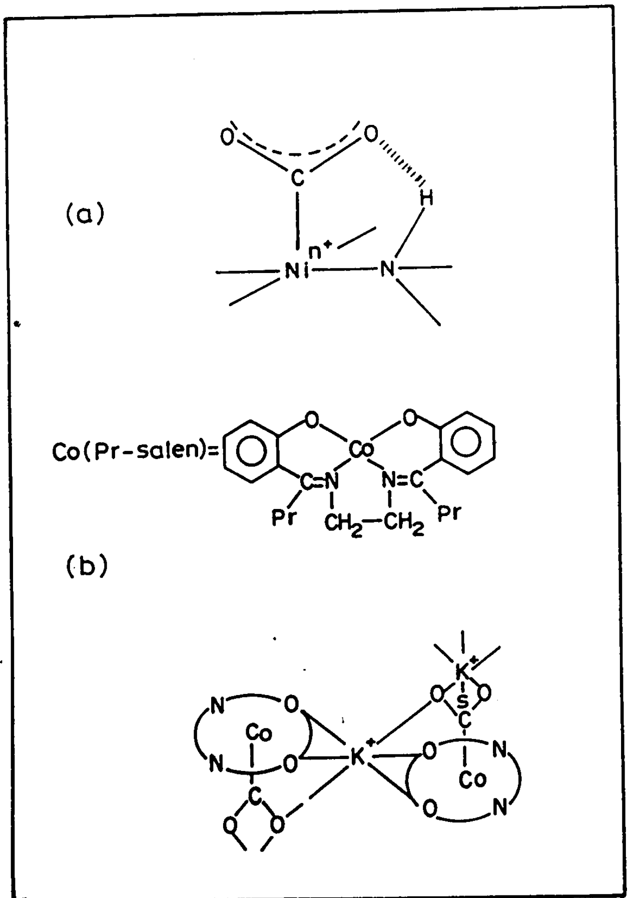


Fig. 13 Intermediate species in the selective reduction (or) binding of CO_2

CO_2 reduction was achieved at -1.30 V with turnover number of the catalyst ~1.1×10^6 h^{-1} and the CO/H_2 ratio ~ 4.2. The high activity was ascribed to the electron-donating BuO- substituents of the complex, which would facilitate the coordination of CO_2 as well as the electron transfer from the complex to the coordinated CO_2 molecule. The use of PVP membrane to disperse the complex decreased the activity. Later Abe *et al.*, in 1997[278] employed a graphite electrode coated with cobalt octacynophthalocyanine (CoPC $(CN)_8$) for electroreduction of CO_2. The most active and selective CO_2 reduction was achieved at -1.20 V (Ag/AgCl) with a ratio of produced CO/H_2 around 10 at pH 9.3. The electrocatalytic CO_2 reduction could be achieved at more positive potential than non-substituted CoPC.

Reaction mechanisms are highly speculative at this stage. CO_2 is coordinated to the metal centre, i.e., a nucleophile, by its electrophilic carbon. The isolation and characterization of CO_2 and CO adducts under different experimental conditions have been reported[272,279-281]. Semiemprical calculations have also contributed to the elucidation of the mechanism. For instance attempts have been made to correlate energy levels in metallophthalocyanine and with their electrocatalytic activity[282]. Such catalytic activity in phthalocynine and tetrasulfonated phthalocyanine complexes appears to the closely related to the possibility of coordinating extra-planar ligands. A factor controlling the binding of these ligands to the metal is the relative energy between the d orbitals of the metallophthalocyanine and the frontier orbital of the extra-planar ligand.

Ab-initio calculations of the coordination of CO_2 to several metals have been reported[283]. The relative stability of different modes of CO_2 coordination was calculated. One of the factors is the bonding between metal atoms and CO_2 in that the ground state has the maximum spin electron configuration. Other high spin states, which only differ from the ground states by electron permutations within the nonbonding d sub shell, must be very close to the ground state. The spin populations show a transfer of one metal valence electron to the CO_2 group, i.e. into a MO largely localized at the sp-hybridized atomic orbital of the carbon atom. Differences in the products of electrocatalysis (CO or CH_4 with some metallophthalocyanines and HCOOH with others) are rationalized on the basis of the electronic configuration of the metal atom. The reduction of CO_2 to CO is attributed to the strongly electron donating HOMO of $[MPc]^{n-}$. This orbital, which derives from the electron-accepting LUMO of neutral MPc, spreads over the nitrogen atoms surrounding the metal atom M. The final step in the generation of CO takes place when it is rapidly separated from the metal M, if this metal has a doubly occupied $2_{a1g}(dz^2)$ orbital. However, if the CO molecule is bound to the metallic atom by σ-bonding, the reduction may proceed up to the CH_4 product. Electron occupation of the LUMO by ionization does not take place in metals with outermost s or p electrons and extensive reduction to CO may not be possible. Electron transfer from MPC to CO_2 will end in CO_2^-, followed by separation of HCOOH instead of CO. In the "carbon dioxide complex" the anion CO_2^- is bent with an angle O-C-O equal to 134° and C is probably σ-bonded using the dz^2 of pz orbitals of M[284].

2.8.2 Porphyrin Complexes

Metalloporphyrins are reported to be active catalysts in the electroreduction of CO_2 to CO in aqueous and non-aqueous media[285]. Cobalt (II)-tetraphenylporphyrin (Co^{II}tpp) fixed on glassy carbon electrodes using 4-aminopyridine, is active toward the electroreduction of CO_2 to CO at potentials 100 mV more positive than water-soluble cobalt (II) porphyrins[83,286]. The overall turnover number exceeded 10^5, in contrast with other systems in which the value is limited to 10^2 [83,287,288]. Water-soluble cobalt porphyrins exhibit catalytic activity towards reduction of CO_2. For instance, when tetraphenylporphyrin (tpp) and octamethylporphyrin (omp) complexes are used, CO is obtained catalytically, whereas palladium and silver porphyrins in dichloromethane (0.1 M TBA^+, BF_4^-) produced oxalate. However, demetallation of the complexes rapidly deactivates the catalyst[289,290]. In these cases, catalytic process was interpreted in terms of the anion radical species of the reduced state of the Pd (II) and Ag (II) porphyrins rather than the Pd (I) and Ag (I) states[274]. 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 (η=90%), with a small amount of HCOOH[291].

Tetraphenylporphyrin iron (III) chloride, with basket-handle of the picket-fence type with secondary amide groups in close vicinity to the porphyrin ring, catalyzes the electrochemical reduction of CO_2 to CO. The cyclic voltammetric studies shows the wave related to the formation of a Fe (O) species[274].

The porphyrin is rapidly consumed in these processes, and the catalysis stops after a few cycles. The degradation of the porphyrin appears to be the result of progressive saturation of the ring through carboxylation and/or hydrogenation. However, the addition of Mg^{2+} or other Lewis acids triggers a spectacular increase in the catalytic efficiency and the stability of the catalyst[274]. Lowering the temperature increases the catalytic efficiency[274].

Catalysis by the complex has been rationalized in terms of the introduction of one molecule of CO_2 into the co-ordination sphere of the iron atom. A carbene-type complex appears as a product when an electron pair is transferred from the iron porphyrin to the CO_2, as shown in Scheme 5. In low temperature, the second step is the addition of another molecule of CO_2 in an acid-base type manner. The C-O bond of the first CO_2 molecule is then broken, forming the Fe^{II} CO complex and a carbonate ion. In the same manner, Mg^{2+} ions can participate earlier in the breaking of the C-O bond. The stability of Fe^{I} CO complex is temperature dependent, and its dissociation becomes more difficult as the temperature is lowered.

Bhugun *et al.*[292], found that the addition of weak Bronsted acids such as 1-propanol, 2-pyrolidone, and CF_3CH_2OH triggers the catalysis of CO_2 reduction by iron (0) tetraphenylporphyrins. Both the catalytic currents and the lifetime of the catalyst increase without significant formation of hydrogen. CO was the main product and HCOOH formed to a lesser extent. Analysis of the reaction kinetics suggested that the action of the acid synergist is to stabilize the initial $Fe^{II}CO_2^{2-}$ carbenoid complex by hydrogen bonding. The formation of a doubly hydrogen bonded complex open the route to the clevage of one of the two C-O bonds resulting in the formation of CO within the iron coordination sphere. The formation of HCOOH involves a reaction pathway where the iron-CO_2 interactions are weaker.

Bhugun *et al.*[293] employed Lewis acid cations such as Mg^{2+}, Ca^{2+}, Ba^{2+}, Li^{+} and Na^{+} to improve the catalysis of CO_2 reduction by iron (0) tetraphenyl porphyrins in terms of catalytic efficiency as well as the lifetime of the catalyst. CO was the main product. It is predicted that electrons are pushed into the CO_2 molecule by the electron-rich catalyst and the cleavage of one of the C-O bonds is helped by the presence of an electron deficient synergist, confirming the role of push-pull mechanism in the catalysis of CO_2 reduction.

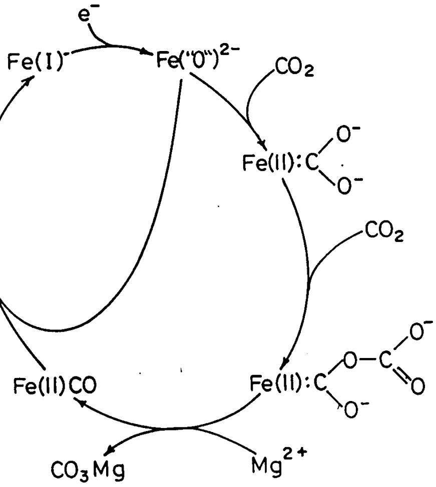
Zhang *et al.*[294] employed a rotating ring (Pt)-disk (graphite) electrode to analyze CO_2 in aqueous solutions. The graphite disk, coated with the complex N, N', N'', N'''- tetramethyltetra-2, 4-pyridoporphyranine cobalt (II) and protected by Nafion® film displays electrocatalytic activities toward CO_2 reduction. The CO generated was thrown on to the Pt ring electrode where it was adsorbed and detected by its electrochemical oxidation. The CO oxidation current at the ring electrode is dependent on CO_2 concentration and the disk electrode potential.

Bakir and Mckenzie[295] studied the electrochemical reactions of CO_2 with *fac*-Re (dpk) $(CO)_3Cl$ (dpk = di-2-pyridylketone) in 0.1M N $(n\text{-}Bu)_4$ PF_6 both in aqueous and non-aqueous media. They found that the electrochemical reactions between CO_2 and *fac*-Re (dpk)$(CO)_3Cl$ are solvent dependent and controlled by the rate of diffusion of electroactive species from the electrode surface.

2.8.3 Metal Complexes of 2-2' Bipyridine and Related Ligands

Several groups have explored the possible use of nickel[296], cobalt[297], rhenium[298-304], ruthenium[305-307], rhodium, iridium and osmium[308] complexes with bipy-type ligands in the electroreduction of CO_2.

Hawecker *et al.*[298-300] had previously shown that [Re (bipy) $(CO)_3Cl$] could be used in photochemical systems of CO_2 reduction for generating CO in the presence of an organic electron donor. Subsequently, it was established that the same complex leads to selective electroreduction of CO_2 to CO at -1.5 V/SCE in DMF-water (9:1v/v). Under given conditions, high faradic

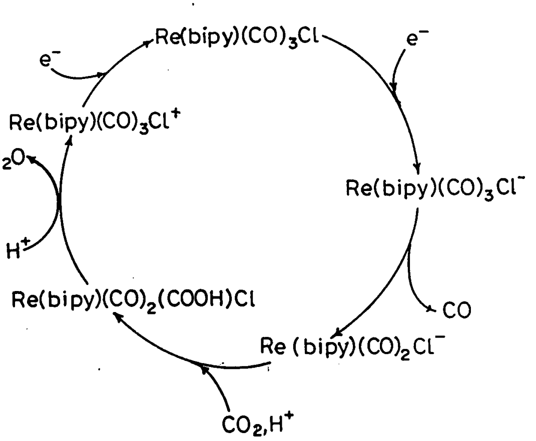


Scheme 5

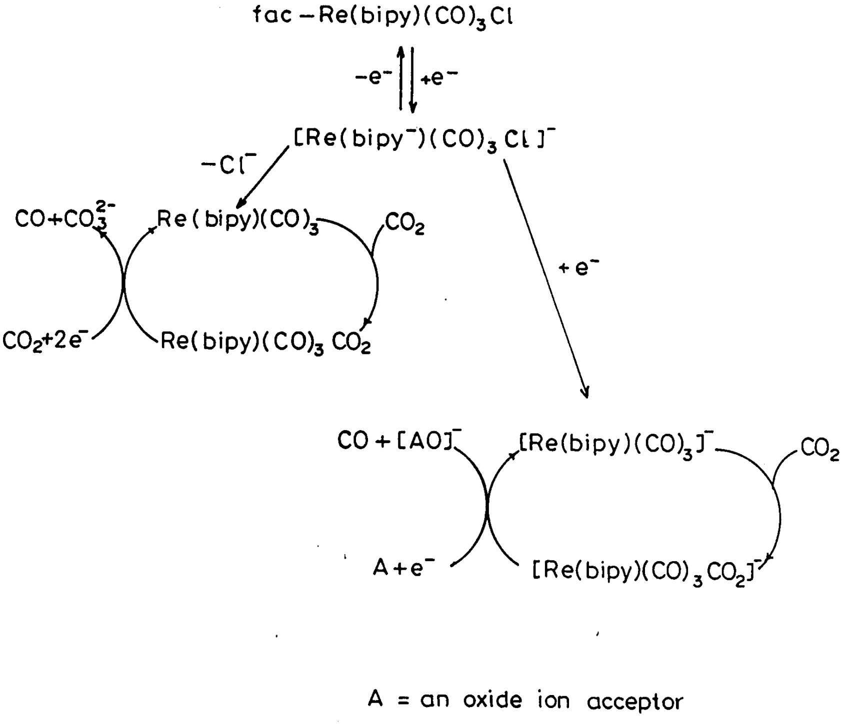
Mechanism of reduction of CO_2 catalyzed by iron porphyrin complex in the presence of Mg^{2+} / other Lewis acids yields (98%) and large overall turnover numbers for rhenium (several hundreds) could be obtained, without significant damage of the system or loss of activity. Experimental factors seem to influence the efficiency and selectivity of the system. In particular, the presence of coordinating ions such as Cl^- is highly favourable, since it prevents the formation of an inactive rhenium (0) dimmer, [*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 presented in Scheme 6.

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 $(CH_3CN)^{301-304}$. 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 operate simultaneously. The common intermediate being the unsaturated species Re(bipy)$(CO)_3^-$. The two proposed pathways of CO_2 reduction are indicated in Scheme 7.

Apart from the rhenium system, the most used and studied complexes in the electrocatalysis of CO_2



Scheme 6
Mechanism of reduction of CO_2 catalyzed by Re (bipy) $(CO)_3$ Cl complex



Scheme 7
Two proposed pathways for the reduction of CO_2 involving a common intermediate

reduction are those of ruthenium (II)[305-307], 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: applied potential, water content, pH and pKa of the acid used as a proton source. It was postulated that 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.

Other rhodium, ruthenium and iridium complexes have been proposed as electrocatalysts for CO_2 reduction to CO or $HCOO^-$, in anhydrous CH_3CN and with $TBuA^+PF_6^-$ as supporting electrolyte[308]. CV experiments performed under CO_2 showed an increase in the current density in the potential range between-1.2 V and -1.7 V/SCE. The complexes such as $Ru(bipy)(COD)^+$, cis-$Rh(bipy)_2(CF_3SO_3)_2^+$, cis-$Ir(bipy)_2(CF_3SO_3)_2^+$, $Ru(\eta^6\text{-}C_6H_6)(bipy)Cl^+$, $Ru(terpy)(dppene)Cl^+$ have been employed. Fine product analysis after electrolysis of CO_2 in the presence of cis-$Rh(bipy)_2$ $(CF_3SO_3)_2^+$ revealed the formation of tri-n-butylamine and 1-butene in addition to HCOO- and H_2. This shows that the supporting electrolyte is partially consumed during the course of the reaction.

The electrochemical reduction of CO_2 by $[Ru(bipy)(terpy)(CO)]^{2+}$ in ethanol + water at low temperatures produced HOCH-CHO and $HOOCCH_2OH$ in addition to CO, HCOOH, HCHO and CH_3OH. The reduction is associated with the stabilization of the Ru-CO bond in $[Ru(bpy)(terpy)(CO)]^{2+}$, $[Ru(bpy)(terpy)(CHO)]^+$ and $[Ru(bpy)(terpy)(COOH)]^+$ under electrolysis conditions. The competitive addition of protons and CO_2 to these complexes results in products with one carbon atom (HCHO and CH_3OH) and with two carbon atoms (HOOCCHO and HOOC CH_2OH)[309-311].

Various rhenium, rhodium and ruthenium complexes have also been used successfully as catalysts in photochemical and electrochemical techniques, either in homogeneous or in heterogeneous catalysts. For instance, it is already known that $[Re(bpy)(CO)_3X]$ [X = Cl^-, Br^-] and its derivatives as efficient catalysts to produce CO both photochemically[298] and electrochemically[299,314,315] in non-aqueous media; However, Yoshida *et al.*[313] in 1993, studied the electrocatalytic reduction of CO_2 by $[Re(bpy)(CO)_3Br]$ as well as $[Re(terpy)(CO)_3Br]$ (terpy = 2,2’: 6’,2"-terpyridine) in an aqueous medium by incorporating them into a coated Nafion membrane, which provides a hydrophobic environment around the catalysts to suppresses proton reduction. The products were CO and HCOOH.

Christensen *et al.*[316] investigated the electroreduction of CO_2 by electrogenerated LNi(0) and $(L^{\bullet -})Ni(0)$ (L=4,4'-dimethyl-2,2-bipyridine, 1,10-phenanthroline) complexes by using *in-situ* FTIR spectroscopy. Electro generated $[L_2Ni]$ reacts slowly with CO_2 to produce $[Ni\ (L)(CO)_2]$; at potentials below -1.6V / SCE, catalytic current of CO_2 reduction was seen and spectroscopic evidence for the transient formation of $[Ni\ (Me_2Bipy^{\bullet -})(CO)_2]$ has been found. It appears that $[Ni\ (Me_2Bipy^{\bullet -})(CO)_2]$ reacts sufficiently fast that its steady state concentration in the thin layer was low. In contrast $[Ni\ (phen^{\bullet -})(CO)_2]$ is more stable. In both cases ‘CO’ was the product found.

Nallas *et al.*[317] found that the electrocatalytic reduction of CO_2 could yield several products depending on the thermodynamic potential applied and the number of electrons transferred. The heteronuclear trimetallic system $\{[(bpy)_2Ru(BL)]_2IrCl_2\}^{5+}$ (where, bpy is 2,2'- bipyridine and BL are the bridging ligands 2,3-bis (2-pyridyl) quinoline (dpq) or 2,3-bis(2-pyridyl) benzoquinoxaline (dpb)), represent a new family of catalyst for the reduction of CO_2. These systems represent a new structural motif. The two remote Ru centres serve to tune the redox properties of the central catalytically active $Ir^{III}(BL)_2Cl_2$ core. Reduction of the iridium metal centre was necessary prior to the onset of catalysis. CPE studies revealed 99% current efficiencies for CO production with high turnover numbers. This is in marked contrast to the lower current efficiency achieved using the monometallic $[Ir(BL)_2Cl_2]^{1+}$ analogs, which produce formate as a reduction product. These catalysts represent a new class of systems in which the redox properties of the catalytic site can be altered through remote metal coordination and variation without a change in the coordination environment of the catalytic iridium site.

Electropolymerized films of vinylterpyridine (v-tpy) complexes of Fe, Ni and Co were employed as electrocatalysts for the reduction of CO_2 by Arana *et al.*[318]. Lam *et al.*[319] demonstrated the formation of CO both in aqueous and nonaqueous media as a product of electroreduction of CO_2 using the complex of

$[CO(qtypy)(OH_2)_2[ClO_4]_2$, $[Ni(qtpy)(MeCN)_2][ClO_4]_2$ at - 1.7 V/SCE in acetonitrile and at -1.3 V/SCE in water with η = 80% and 35% respectively.

Sende *et al.*[320] employed 4-vinyl and 6-vinylterpyridine (4-vtpy; 6-vtpy) complexes of Cr, Ni, Co, Fe, Ru and Os and HCOOH was found to be the product. The results are given in Table VIII. Hossain *et al.*[321] employed a series of $[PdCl_2L_2)$ complexes (L-substituted pyridine and pyrazole) as electrocatalysts for the reduction of CO_2 in acetonitrile containing 0.1 M TEAP at glassy carbon or Pt electrodes. The complexes were $(PdCl_2L_2)$ [L = pyrazole (pyra), 4-methylpryidine (4-Mpy) and 3-methylpyrazole (3-Mpyra) at an applied potential of -1.10 V/Ag/10 mM Ag^+ and the reduction products were formic acid and H_2 with no CO. The current efficiency for the formation of HCOOH was 10,20 and 10.2% for Pd complexes of pyra, 4-Mpy and 3-Mpyra respectively. The current efficiency for the H_2 evolution was 31-54% and the source of the formate proton and H_2 was from the added water (4% by volume).

Wong *et al.*[322] studied the effect of four weak Bronsted acids such as 2,2,2-trifluoroethanol, phenol, methanol and water on the electrocatalytic reduction of CO_2 by $[Re (bpy)(CO)_3(py)]^{2+}$ in acetonitrile. The addition of weak Bronsted acids enhances the rate of the catalytic process and improves the lifetime of the rhenium catalyst and CO was found to be the only product with faradaic efficiency of 100%. Ali *et al.*[323] investigated electroreduction of CO_2 employing 2,2' bis (1-methylbenzimidazol-2-yl)-4,4'-bipyridine (dmbbbpy), and unsymmetrical chelating ligand into a Ru $(bpy)_2$ moiety with the aim of creating reaction sites by opening the chelating ring and to accumulate the electrons into the ligand required in the reduction of CO_2. The products were found to be HCOOH with trace amounts of CO and $C_2O_4^{2-}$ in the presence and absence of H_2O respectively, in MeCN.

2.8.4 Phosphine Complexes

It is paradoxical to see that the numerous phosphine complexes known and extensively employed in homogeneous catalysis (hydrogenation, hydroformylation and hydrosilylation of olefins etc.,) have been very little used as electrocatalysts for CO_2 reduction. Interestingly, the vast majority of isolated and crystallographically characterized CO_2 complexes of various transition metals[324-330] contain phosphines or arsines as ancillary ligands.

Rh $(diphos)_2Cl$ has been used in anhydrous CH_3CN[331], at -1.55 V/Ag wire; $HCOO^-$ was 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 tested in acidified CH_3CN[332]. The palladium complexes showed some catalytic activity, where as 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 (0.5h).

Christensen and Higgins[333] have shown that CO_2 is reduced to oxalate with high selectivity at potentials <-1.1V vs. SCE at a PVA/(Ni $(dppm)_2Cl_2$]-coated Pt electrode in acetonitrile in a thin layer cell. At -1.8 V, about 70%-90% of the CO_2 lost was converted to oxalate, with a turnover number of 5-6 before all the CO_2 in the thin layer was consumed. When the $[Ni(dppm)_2Cl_2]$ is employed in acetonitrile in solution form, no oxalate is observed. Instead, in the presence of adventitious water, the major process appears to be the dissolution of CO_2 to CO_3^{2-}, with the formation of a small amount of formate. Once all the water was removed, the mechanism changed, and CO_2 is produced. However, the participation of $[Ni(dppm)_2Cl_2]$ in catalytic process is not well established.

2.8.5 Metal Clusters and Other Polymetallic Complexes

Notable systems in this category are: 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[334] that CO_2 is electroreduced at about -2.0 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 tetra nuclear cluster. Owing to the very negative potential applied, it was postulated that the tetraalkylammonium salt, which was used as the supporting electrolyte, provides the proton required in the reaction. Later, the same group extended their investigations to other 4Fe-4S clusters by replacing the benzyl thiolate initially used by $t\text{-}BuS^-$

Table VIII

Summary of Transition Metal Complexes Used for Electrocatalytic Reduction of CO_2

Catalyst	Electrode	Solvent	Products	Reference
$[CoL]^{2+}$	GC	$MeCN\text{-}H_2O$	CO, H_2	364a
L = 14-membered tetraaza				
macrocylic ligands	GC	$DMF\text{-}H_2O$	CO, H_2	364a
$[Ni(cyclam))]^{2+}$	Hg	H_2O	CO	355,287
[Ti(pc)]	$C_{\text{based gas diff.}}$	H_2O	CO	273,284
[Fe(pc)]	$C_{\text{based gas diff.}}$	H_2O	CO	273,284
[Co(pc)]	C_{modified}	H_2O	$HCOO^-$	267,268
	C_{modified}	H_2O	CO, H_2	271
[Ni(pc)]	GC	H_2O	$HCOO^-$	268
[Cu(pc)Cl]	$C_{\text{based gas diff.}}$	H_2O	CO	284
[Co(TMPP)]	GC_{modified}	H_2O	CO, HCOOH	291
[Co(TPP)]	GC_{modified}	CH_2Cl_2	CO	285
[Pd(TPP)]	GC_{modified}	CH_2Cl_2	$C_2O_4^{2-}$	289
$[Fe_4S_4(SCH_2Ph)_4]^{2-}$	Hg	DMF	$HCOO^-$	335a
$[Fe_4S_4(SXN\text{-})_4]^{2-}$				
$(X\text{=-}COCM_2\text{-},$				
$\text{-}COC_6H_4CH_2)$	Hg	DMF	$HCOO^-$	335b
$[Re(CO)_3Cl(bipy)]$	GC	$DMF\text{-}H_2O$	CO	298-300
$[Re(CO)_3Cl(vbipy)]$	Pt	MeCN	CO, CO_3^{2-}	302,304
$[Re(CO)_3Cl(bipy\text{-}py)]$	Pt	MeCN	CO	314b
$[M(L)_2]^{2+}$, M=Fe, Co, Ni				
L= dapa, vtpy, tptz, tppz, tpy,tpen	Pt	MeCN	CO	318a
$[Ru(bipy)_2(CO)_2]^{2+}$	Hg	$MeCN\text{-}H_2O$	CO	320b
		$MeCN\text{-}CH_3OH$	CO, $HCOO^-$	320b
$[Ru(bipy)(dmbipy)(CO)_2]^{2+}$	Hg	$MeCN\text{-}H_2O$	CO	320b
		$MeCN\text{-}CH_3OH$	CO, $HCOO^-$	320b
$[Ru(dmbipy)_2(CO)_2]^{2+}$	Hg	$MeCN\text{-}H_2O$	CO	320b
		$MeCN\text{-}CH_3OH$	CO, $HCOO^-$	320b
$[Fe(vtpy)_2]^{2+}$	Pt	MeCN	CO	318b
$[Ru(CO)_2(bipy)_2]^{2+}$	Hg	$DMF\text{-}H_2O$	$HCOO^-$, CO	305-307
cis-$[Ru(CH_2Ph)CO(bipy)_2]^+$	Hg	MeCN	CO	304
$[(\eta^6\text{-}C_6H_6)Ru(bipy)Cl]^+$	Pt	MeCN	CO, $HCOO^-$	308a
$[Ru(terpy)(dppe)Cl]^+$	Pt	MeCN	CO, $HCOO^-$	308a
cis-$[OsH(CO)(bipy)_2]^+$	Hg	MeCN	CO	304
		$MeCN\text{-}H_2O$	CO, $HCOO^-$	
cis-$[Os(Me)(CO)(bipy)_2]^+$	Hg	MeCN	CO	304
cis-$[Os(Ph)(CO)(bipy)_2]^+$	Hg	MeCN	CO	304
$[Co(vtpy)_2]^{2+}$	Pt	MeCN	HCOOH	318a
$[Cr(4\text{-}vtpy)_2]$	GC_{modified}	H_2O	HCHO	320a
$[Ru(4\text{-}vtpy)_2]$	GC_{modified}	H_2O	HCHO	320a
$[Os(4\text{-}vtpy)_2]$	GC_{modified}	H_2O	HCHO	320a
$[Rh(COD)(bipy)]^+$	Pt	MeCN	CO, $HCOO^-$	308a
cis-$[Rh(bipy)_2(CF_3SO_3)_2]^+$	Pt	MeCN	CO, $HCOO^-$	308a,308b
cis-$[Ir(bipy)_2(CF_3SO_3)_2]^+$	Pt	MeCN	CO, $HCOO^-$	308a, 308b
$[Ni(vtpy)_2]^{2+}$	Pt	MeCN	HCOOH	318a
$[Ni(bipy)_3]^{2+}$	Pt/GC	DMF	CO	296
[RhCl(dppe)]	Hg	MeCN	$HCOO^-$	331a
$[Rh(CO)Cl(PPh_3)_2]$	Hg	DMF	CO	331b
$[Ir(CO)Cl(PPh_3)_2]$	Hg	DMF	CO	331b
$[Ni(MeCN)_4(PPh_3)_2]^{2+}$	Pt/GC	DMF	CO	296
$[Ni_3(\mu\text{-}CNMe)(\mu_3\text{-}I)(dppm)_3]^+$	Hg	THF	CO, CO_3^{2-}	339b
$[Pd(triphos)(PPh_3)]$	GC	MeCN	CO, H_2	332
$[Pd(triphos)(Pet_3)]$	GC	MeCN	CO, H_2	332
$[Pd(triphos)\{P(OMe_3)\}]$	GC	MeCN	CO, H_2	332

and PhS^- [335]. In addition, mixed clusters (Mo-Fe-S or W-Fe-S) were also tested. But, under the electrolysis conditions used (-2.0 V/SCE) the cluster structures were rapidly destroyed.

Intriguing results[229] were reported on the electroreduction of CO_2 to methanol[336-338]. Although mechanistic considerations are highly speculative at this 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 co-solvent, making the estimation of the CH_3OH produced particularly difficult and inaccurate.

Tomohiro *et al.*[339a] employed Fe_4S_4 cubane clusters bearing a 36-membered methylene backbone in DMF (0.1M $[Bu^n_4N][BF_4]$) for the electroreduction of CO_2 and found formate as the only product formed with the faradaic efficiency of 23-40%. Tert-butyl and benzyl type macrocyclic Fe-S derivatives are found to be several times more efficient than conventional clusters bearing small thiolate ring. The structure of the compound is given in Fig. 14.

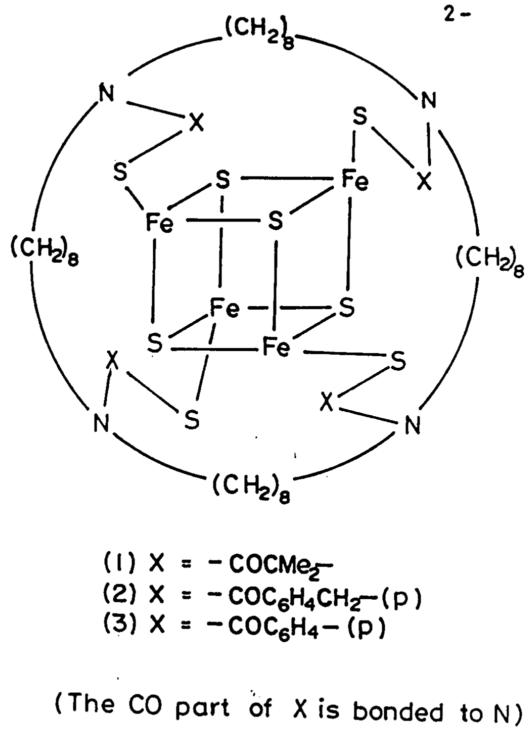


Fig 14 Structure of Fe_4S_4 cubane clusters bearing 36- member methylene backbone

Cluster complex such as $[Ni_3(\mu_3\text{-I})(\mu_3\text{-CNMe})(\mu_2\text{- dppm})_3]$ was employed to electrolyze the reductive disproportionation of CO_2 to CO and CO_3^{2-} (in 'wet' solvents HCO_2^- is formed)[339b].

Ogura and Takamagari[336] employed Everitt's salt, $K_2Fe^{II}[Fe^{II}(CN)_6]$ for the conversion of CO_2 to methanol in the presence of various metal complexes and primary alcohols in 0.1 M KCl. The metal complexes employed were diaquabis (oxalato) chromate (III), $K[Cr(C_2O_4)_2(CH_2O)_2]$, aquapentacyanoferate (II), $Na_3[Fe(CN)_5(H_2O)]$, aquapentachlorochromate (III),$[NH_4]_2$, $[Cr\text{-}Cl_5(H_2O)]$ and bis-(4,5-dihydroxybenze-1,3-disulphonate) ferrate (III), $[Fe\{C_6H_2)(OH)_2(SO_3)_2\}_2]^-$. The activation energies for the methanol formation were in the range 5.8 -10.6 Kcal / mol, approximately twice those for the reduction of CO. The IR spectra of the metal complexes indicated that the reduction of CO_2 takes place via a formate-type intermediate. The mechanism is considered to be very similar to that for reduction of CO, but the reduction of CO_2 appear to be more dominated by its insertion into a M (central metal) - OR (primary alcohol) bond than is that of CO.

In order to reduce the over potential required for the electrochemical reduction of CO_2, a metal complex - fixed polyaniline (PAn) / Prussian blue (PB)-modified electrode has been developed by Ogura *et al.*[340] and the role of two laminated films and a fixed metal complex were discussed in detail. The onset potential for the reduction of CO_2 to lactic acid, a major product is close to the thermodynamic value (E° = 0.20 V/SCE). The metal complex acting as the catalyst is a large aromatic anion, which is bound to the conducting polymer through π-interaction and not undoped during the cathodic polarization. The existence of R-OH > CH-OH >, R-COOH and -CO-NH- groups in the coated film was confirmed by FTIR spectroscopy, supporting the involvement of the observed products (lactic acid, formic acid, MeOH, EtOH etc.). A cause for the generation of C_3 species such as lactic acid may be due to the bifunctional activation of CO_2 in which the electrophilic carbon atom links to the amino group of PAn and the basic oxygen atom coordinates to the central metal of the complex.

Ogura *et al.*[341] in their latter studies employed *in-situ* FTIR spectroscopy to investigate the nature of a metal complex immobilized polyaniline (PAn)/ Prussian blue-modified electrode for the electroreduction of CO_2 in an aqueous solution of 0.1 M KCl. During cathodic polarization, the ring structure of PAn transformed from quinoid to benzenoid states. It was confirmed that the metal complex [1,8-

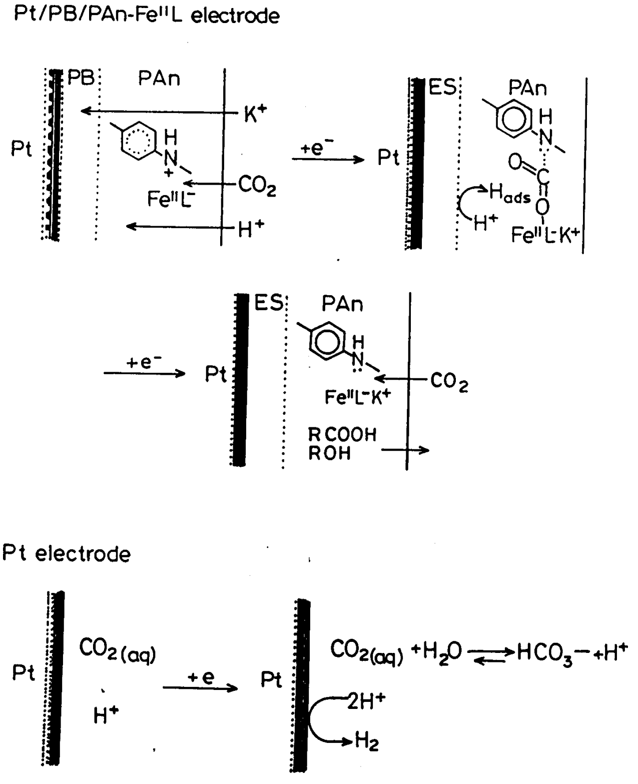
dihydroxynaphthalene-3,6-disulfanato iron(II)] once doped on to the conducting polymer is not undoped in cathodic processes, and the charge balance of the polymer is kept by taking an electrolyte cation in or out. The onset potential where CO_2 was accumulated with the modified electrode was O V/Ag-AgCl and the amount of CO_2 on the electrode was largest at -0.2 V. The accumulation of CO_2 with the electrode mediator was caused by the bonding between the mediated PAn and CO_2 through a linkage of the electrophilic carbon atom of CO_2 with the nitrogen atom of the benzenoid ring. The prolonged electrolysis of CO_2 at potentials more negative than -3.0 V led to the generation of $C_1 \sim C_3$ species involving lactic and forming acids and the pathway for the initial reduction process was proposed.

Ogura *et al.*[342], carried out mechanistic studies of CO_2 reduction on mediated electrode with conducting polymer and inorganic conductor films (PAn/prussion blue) using long-term electrolysis, liquid chromatography/mass spectroscopy (LC / MS) and *in-situ* FTIR reflection absorption spectroscopy. It was demonstrated that CO_2 could be reduced to organic acids and alcohols by the reaction with H_{ads} atoms on the Pt/PB/PAn-Fe^{II}L electrode. The schematic representation of the electrode reactions is depicted in Scheme 8. Lactic, acetic and formic acids, methanol and ethanol were identified as the main products. The formation of -CO. NH-bonding in the reduction of CO_2 was confirmed from *in-situ* FTIR spectra (1657, 1538 cm^{-1}) and it was indicated that CO_2 was bifunctionally activated by combining the carbon atom with the amino group of PAn and the oxygen atom with the central metal of the complex.

2.8.6 Biphenanthrolinic Hexaazacyclophane Complexes

Little is known about the other systems containing extended π-electron orbitals and differing from the phthalocyanines and porphyrins. Since hexazacyclophanes can be considered as relatives of the PCs and PPys, they may also be catalysts in numerous reactions. Preparative procedures for some of the azacyclophanes have been reported[343-348]. Studies of the chemical properties of azacyclophanes, which are hexaazacyclophane macrocyclic complexes derived from 1,10-phenanthroline, demonstrated that they are promising catalysts for CO_2 reduction.

Large-scale preparations of hexa-azamacrocyclic ligand, which is a diazabridging biphenanthrolinic macrocyclic ligand, and its Cu (II), Ni (II) and Co (II) complexes, have been reported[349]. Electrochemistry in a CO_2 atmosphere in dimethylformamide demonstrates a high electrocatalytic activity for the reduction of CO_2. The waves for CO_2 reduction mediated by these complexes observed at about -0.80 V/SCE occur at the most positive potentials recorded for these electrocatalytic processes[350]. Reductions of CO_2 occur close to the region involving the metal reduction process. The current intensity remains constant during prolonged electrolysis of the Ni derivative in CO_2 at the catalytic peak potential; the reduction products analyzed by current ratios but the results were not well understood[349]. Pulsed radiolysis studies[349,351] suggest that CO_2 adducts could be formed during the reduction process observed in the Cu (II) complex. Semi-empirical self-consistent field and CI calculations of INDO type have been applied to the analysis of the electronic transitions of hexaazacylophane[350,352]. The results confirm the activity of the structures toward electrochemical reduction processes involving the metal centre.



Scheme 8

Schematic representation of the electrode reactions involving CO_2 at Pt/PB/PAn-Fe^{II}L and bare Pt electrodes108a

2.8.7 *Aza-macrocyclic Complexes*

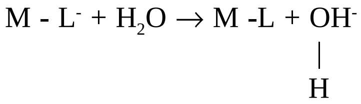
Many of the tetraazamacrocyclic complexes synthesized in the past three decades display structural analogies with metalloporphyrins[353]. In particular, square-planar geometries are highly favoured with the possibility of coordinating additional ligands on the axial positions. However, the electronic properties of porphyrins are usually different from those of other synthetic tetraazamacrocyclic ligands[354]. The overall charge borne by the ligand is -2 for porphyrines (and phthalocyanines) 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 understand 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 orbitals for instance) the substrate to be reduced should 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 orbital 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.

$$M - L \xrightarrow{e^-} [M\text{-}L]^- \qquad \dots(45)$$

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

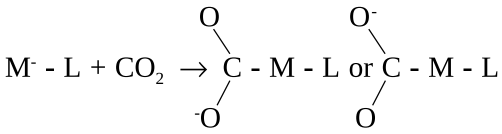
$$M\text{-}L^- + CO_2 \rightarrow M\text{-}\underset{\substack{|\\ COO^-}}{L} \qquad ...(46)$$

(Or)

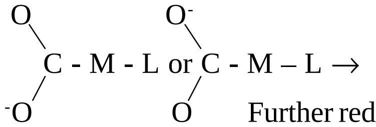


$$M - L^- + H_2O \rightarrow M\text{-}\underset{\substack{|\\ H}}{L} + OH^- \qquad ...(47)$$

The metal localized reduction is,



$$M^- - L + CO_2 \rightarrow \overset{O}{\underset{^-O}{C}} - M - L \text{ or } \overset{O^-}{\underset{O}{C}} - M - L \qquad ...(48)$$



$$\overset{O}{\underset{^-O}{C}} - M - L \text{ or } \overset{O^-}{\underset{O}{C}} - M - L \rightarrow \text{Further reduction, leading to effective } CO_2 \text{ reduction} \qquad ...(49)$$

Further reduction,
leading to effective
CO_2 reduction ...(49)

$M^- - L + H_2O \rightarrow H - M - L + OH^-$ ...(50)

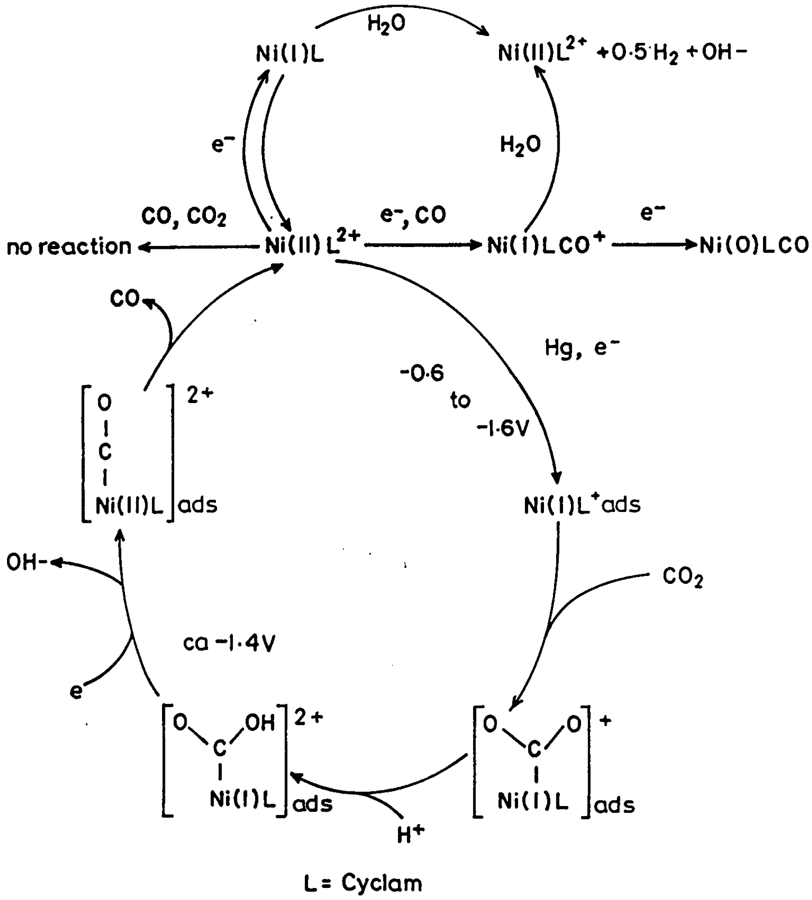
H - M - L → Further reduction, protonation, insertion etc. leading to H_2 production or CO_2 hydrogenation

The complex of Ni (II) and CO (II) with the macrocyclic ligand cyclam (1,4,8,11-tetraazcyclotetradecane) have been shown to be particularly effective and selective catalyst for the electrochemical reduction of CO_2 to CO at mercury electrodes in water, at potentials much less negative than those required for the uncatalyzed reduction[102,356,357,287]. The ability of $[Ni\ (cyclam)]^{2+}$ to serve as a catalyst precursor for the electroreduction of CO_2 has prompted numerous studies on the electrochemistry of this complex. The key findings are:

1. The active catalyst is a form of $[Ni(cyclam)]^+$ adsorbed on the surface of mercury electrodes[287,355,356,358,359].
2. $[Ni(cyclam)]^+$ is adsorbed on mercury over an unusually wide potential range, including potentials that are much more positive than those where $[Ni(cyclam)]^{2+}$ is reduced to unadsorbed[359,360] $[Ni(cyclam)]^+$.
3. CO is the product of the catalyzed reduction of CO_2.

Theoretical calculations[361] predicted that the adsorbed Ni complex is $[Ni\ (cyclam)]_{ads}^+$; but the same complex in solution is not catalytically active towards the reduction of CO_2. The catalytic activity is severally diminished in the presence of CO on unstirred mercury electrodes and, as CO is the primary product of the reduction, this behaviour limits the long-term effectiveness of the catalyst. The decrease in activity is proposed due to the formation of an insoluble complex of Ni (0), i.e., [Ni (cyclam) CO], the intermediate product formed during the electroreduction of CO_2. Unfavourable shifts in the potential and decreased catalytic activity were observed when carbon rather than mercury was used as a working electrode with $(Ni\ (cyclam)]^{2+}$ as the catalyst.

Mechanisms for the electrochemical processes at mercury electrodes in solutions of $[Ni(cyclam)]^{2+}$ and CO_2 have been proposed[312,360,363] as shown in Scheme 9. It shows the formation of a carbon-bonded Ni (II)



Scheme 9

Mechanism of reduction of CO_2 catalyzed by [Ni (cyclam)]$^{2+}$ complex

complex by reaction of CO_2 with [Ni (cyclam)]$^{+}$. The formation of such a complex is considered to be a fundamental step in the mechanism of the Ni (cyclam)$^{2+}$ - catalyzed electrochemical reaction[312]. The overall process for the transformation of CO_2 into CO also involves inner-sphere reorganization. This scheme 9 also shows the formation of a sparingly soluble complex containing Ni (0), cyclam and CO, which is a product of the reaction of [Ni (cyclam)]$^{2+}$ under CO. Deposition of a precipitate of the Ni (0) complex on the mercury electrodes inhibits the catalysis and removes the catalyst from the cycle. The potential at which the [Ni^{I}L-CO_2H]$^{2+}$ intermediate accepts electrons from the electrode is not affected by substitution on the cyclam ring, as shown by comparison of [Ni(cyclam)]$^{2+}$ and [Ni(TMC)]$^{2+}$; (TMC = tetra-N-methylcyclam) as catalysts[359]. However, the catalytic activity of [NiL] (L=5,7,7,12,14,14,hexamethyl-1,4,8,11-tetraazacyclotetradecane) can be strongly reduced.

The presence of carbonylated complexes of Nickel (I) during the reaction was clearly demonstrated by spectroscopic methods (UV-visible, IR, EPR), either in aqueous media or in DMF. These compounds correspond to the three-electron reduction products of Ni (cyclam)$^{2+}$ and CO_2.

$$Ni^{II}(cyclam)^{2+} + CO_2 + 3e^- + 2H^+ \rightarrow Ni^{I}(CO)cyclam^+ + H_2O \quad ...(51)$$

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.

Schmidt *et al.*[364a] investigated the effects of redox potential, steric configuration, solvent and alkali metal cations on the binding of CO_2 to Co (I) and Ni (I) macrocycles and arrived at the following conclusions.

a) The binding of CO_2 to Co (I) macrocyclic complexes followed predictable trends in metal basicity, which was reflected in Co (II)/Co (I) redox potentials.

b) Steric factors have large effect on binding strength of CO_2 to Co macrocyclic complexes suggesting that H-bonding and/or steric bulk might be an important factor in CO_2 binding.

c) For nonprotic solvents the strength of CO_2 binding was weakly correlated with solvent dielectric constants. This is attributed to the differences in the solvation of CO_2 and ion paring in the most nonpolar solvents.

d) The role of alkali metal cations in stabilizing CO_2 adducts of Co (salen) complexes was quantified and was found to be more important for CO_2 binding to these complexes than for CO_2 binding to the cobalt tetraazamacrocycles.

Fujita *et al.*[365] studied a series of (14 member) macrocyles probing the factors governing the binding of CO and CO_2 to the square planar, low spin d^8 Co (I) metal centres. The CO-binding constants increases from 5 x 10^{-4} to > 3 x 10^{-8} M^{-1} as the CoL^{2+}/CoL^+ reduction potential drops from -0.34 to -1.65 V/SCE, the CO stretching frequencies decrease as the binding constants increase, confirming the importance of back-bonding to the binding. Similarly, charge transfer from cobalt to CO_2 is an important factor in stabilizing the CO_2 adducts. The H-bonding interactions between the bound CO_2 and amine macrocycle N-H protons may serve to additionally stabilize the adduct, while steric repulsions by the macrocycle methyl groups destabilize the adducts.

Rotating-copper-disk electrode technique has been used to evaluate the efficiency of the nickel macrocyclic catalyst for the reduction of CO_2 to CO. Investigations have been carried out using $Ni(diazacyclam)^{2+}$ (diazacyclam=3,10-dimethyl-1,3,5,8,10,12-hexaazacyclodecane), a complex derived from cyclam, which appears to be more active than $[Ni(cyclam)]^{2+}$ under the same conditions[312,362]. There results are consistent with the mechanistic reports of the other authors[312,355,287].

An *ab-initio* MO-SDCI study of model complexes of the intermediates in the electrochemical reduction of CO_2 catalyzed by $NiCl_2$(cyclam)[361] and calculations on several Ni^I and Ni^{II}-CO_2 complexes indicate that CO_2 can coordinate to $Ni^IF(NH_3)_4$, yielding a stable Ni-CO_2 complex, but not to $[Ni^{II}F(NH_3)_4]^+$, $[Ni^{II}F(NH_3)_4]^+$ or $[Ni^I(NH_3)_5]$ [361]. The HOMO of $Ni^IF(NH_3)_4$ (η'-CO_2) is largely the oxygen pπ-orbital and lies at a higher energy than the HOMO (nonbonding π orbital) of the uncomplexed CO_2. In addition, the electron density increases around the oxygen atom upon CO_2 coordination. As a result, the coordinated CO_2 in $Ni^IF(NH_3)_4$ (η'-CO_2) is activated with regard to electrophilic attack and is expected to undergo facile protonation.

MO calculations also show that the second one-electron reduction can easily occur in the protonated species $[NiF (NH_4)_3(CO_2H)]^+$, yielding the triplet state $[NiF(NH_3)_4(CO_2H)]$, but cannot occur in the unprotonated species $NiF(NH_3)_4(CO_2)$. The second reduction noticeably weakens the C-OH bond, suggesting that OH^- easily dissociates from $[NiF(NH_3)_4(CO_2H)]$, yielding the triplet state of $[Ni^{II}F(NH_3)_4(CO)]^+$. The CO bond to Ni(II) is calculated to be weak, which suggests that CO easily dissociates from Ni(II). All these results support a reaction mechanism proposed by Collin *et al.*[312] for the electroreduction of CO_2 electrocatalyzed by $NiCl_2$(cyclam).

A series of new mono-, di- and tetra fluorinated cyclams have been prepared their activity towards the eletrocatalytic reduction of CO_2 showed that the efficiency of (CO + H_2), product yields and the H_2/CO selectivity depend upon the number of fluorine atoms available. The tetra fluorinated complex shows more efficiency and selectivity at potentials lower than those measured for some nonfluorinated cyclam complexes[366].

The CO yields decreases as the number of fluorine atoms increases[366]. However, at a potential of -1.10 V, $[Ni^{II}$(3,3,10,10-tetrafluoro-cyclam)$](ClO_4)_2$ showed more efficient selective catalytic activity than the nonfluorinated [Ni(cyclam)] Cl_2 complex. The perchlorate complex may have a higher catalytic efficiency than the chloride complex at a higher potential (-1.3 V). There are results, which reveal the stereochemical effect of substituents on the electrocatalytic reduction of CO_2. The complexes of RSSR-Ni(2,3,9,10-tetramethyl-cyclam)$^{2+}$, RRSS-Ni(2,3,9,10-tetramethyl cyclam)$^{2+}$ and Ni(5,12-dimethyl-cyclam)$^{2+}$ in aqueous KCl solution display increases in the catalytic current by a factor of 50-100, with the current densities of the RRSS-Ni(2,3,9,10-tetramethyl-cyclam)$^{2+}$ and Ni(5,12,-dimethyl-cyclam)$^{2+}$ complexes being higher than that observed for $[Ni(cyclam)^{2+}]$[367].

Thus, these complexes appear to be "better" catalysts than $Ni(cyclam)^{2+}$ in terms of their larger catalytic currents and more positive potentials. Hydrogen and formate production is less than 1.5% of the CO for each mole of complex. However, the geometric isomer RSSR - Ni (2,3,9,10-tetramethylcyclam)$^{2+}$ shows a lower catalytic activity because the axial methyl groups may sterically hinder CO_2 coordination. Experimental observations reported for Ni (cyclam)$^{2+}$ in DMSO, and for RSSR - Ni (2,3,9,10-tetramethyl cyclam)$^{2+}$, RRSS-Ni(2,3,9,10-tetramethylcyclam)$^{2+}$ and Ni(5,12-dimethyl cyclam)$^{2+}$ in acetonitrile[365] revealed that catalytic activity has not been observed in aprotic solvents, because the reaction requires a proton source. Abba *et al.*[368] prepared a wide range of functionalized azacyclam complexes of Ni^{II} and found that water-soluble Ni^{II} azacyclam complexes catalyze the electroreduction of CO_2 and with efficiency comparable to that of $[Ni^{II}(cyclam)]^{2+}$. Such a high efficiency is strictly related to the structural features of the cyclam and azacyclam framework.

Geometrical factors could also determine the selective properties of Ni (cyclam)$^{2+}$. Intermediate species as represented in Fig. 13b might be able to explain why CO_2 is so selectively reduced in the presence of water as solvent. It was 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 previous by been observed in the reaction of cobalt (I) complexes with CO_2 [369]. 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[369].

Hay *et al.*[370] found that the Ni (II) complex of N-hydroxy ethylazacyclam [3-(2'-hydroxy ethyl)-1,3,5,8,12-petaazacyclotetradecane electrocatalyzes CO_2 reduction. This complex was less active for hydrogen evolution in an acetate electrolyte than [Ni (cyclam)]$^{2+}$ and thus appeared to be more active than the cyclam complex for CO_2 reduction, under the same experimental conditions.

Bujno *et al.*[371] have employed isomers of a tetraazamacrocyclic Ni(II) complex in solutions saturated with argon, CO and CO_2. The complex chosen was [Ni(CRH)]$^{2+}$. Isomers of [Ni(CRH)]$^{2+}$ have been isolated and studied using dc and ac voltammetry on Hg electrodes in aqueous solution. The configurational isomerism of this complex can lead to a difference in the adsorbability of the complex and changes in the electrode behaviour resulting from the transition of one configurational isomer into another, more stable one under experimental conditions.

Kelly *et al.*[372] in 1995 studied the kinetics and thermodynamics of CO_2 and H^+ binding to Ni(cyclam)$^+$ in aqueous solution using pulse radiolysis and laser flash photolysis. Reduction of Ni (cyclam)$^{2+}$ by both $H^\bullet$ and $CO_2^{\bullet-}$ has been shown to proceed by an inner sphere mechanism. The adducts thus formed [Ni(cyclam)(H)]$^{2+}$ or [Ni(cyclam)(CO_2)]$^+$, rapidly come to equilibrium with free Ni(cyclam)$^+$ and H^+ or CO_2. The binding of CO_2 does not proceed by insertion into a Ni-H bond. The species [Ni(cyclam)(H)]$^{2+}$ and [Ni(cyclam)(CO_2)]$^+$ are proposed to be intermediates in the two electron reduction of H^+ and CO_2 by Ni(cyclam)$^+$. Binding constants for the addition of protons and CO_2 to Ni(cyclam)$^+$ reveal that the formation of the CO_2 adduct is favoured in CO_2 saturated solution at $pH > 2.0$. It is this property that is responsible for the exceptional selectivity for CO_2 reduction over H^+ reduction by Ni(cyclam)$^+$ at pH 4. However, the origin of the efficiency by which Ni (cyclam)$^+$ reduces CO_2 is not clearly established.

Bujno *et al.*[373] in their latter study, investigated the mechanism of electropoisoning in the reduction of CO_2 catalyzed by [Ni(CRH)]$^{2+}$ and [Ni(cyclam)]$^{2+}$ using cyclic and stripping dc voltammetry. In both cases, the product of CO_2 reduction is CO, which undergoes further catalyst reaction with the Ni(I) form of the catalyst. It was proposed that the decay of the catalytic activity was attributed to the formation of Ni(0) carbonyl compound blocking the surface of the electrode.

Majerikskaia *et al.*[374] in 1997 studied the electroreduction of CO_2 catalyzed by 1,4,7,10-tetramethyl-1,4,7,10- tetraazacyclodoecane Ni(II) as a electron relay catalyst. It was found that photolysis of a mixture of $[Ni(Me_4[12]aneN_4)\ (H_2O)]^{2+}$, $[Ru(bipy)_3]^{2+}$, ascorbate and CO_2 resulted in the formation of CO, hydrogen and formic acid. The electrolysis of $[Ni(Me_4[12]aneN_4)(H_2O)]^{2+}$ in the presence of CO_2 and various electrolytes resulted in the formation of formic acid. The electrolysis of $[Ni(Me_4[12]aneN_4)\ (H_2O)]^{2+}$ in the presence of CO_2 and various electrolytes resulted in the formation of formic acid. This complex, preferentially reduces CO_2 versus a proton in aqueous solution regardless of whether this Ni (I) complex generated electrochemically or photochemically.

Ragini *et al.*[375] and Aulice Scibioh *et al.*[376-379] investigated the electrochemical reduction of CO_2 using a series of nickel azamacrocycles as electrocatalysts at hanging mercury drop electrode in aqueous and aqueous mixtures of organic solvents. In the potential range between –1.25 to –1.46 V/SCE, the products were found to be CO and H_2 in 2:1 mole ratio in gaseous phase and trace amounts of HCOOH was found in solution phase.

The effect on pH, supporting electrolytes, solvents and size of the macrocyclic ring and substituents on the macrocyclic ring seems to influence the optimization of product selectivity.

Alwis *et al.*[380] recently employed two series of binuclear macrocylic Ni (II) complexes with varying length of chain linking between the two-macrocyclic rings as electrocatalyst for the reduction of CO_2. The first series consisted of binuclear complexes containing polyazamacrocycles with $(CH_2)_n$ bridges (n=2,3,4,6) or a p-xylyl linkage. The two-nickel sites in the binuclear complexes behaved independently with the currents corresponding to the simultaneous transfer of two electrons. The redox potentials are constant along the series, while the peak separation increased reflecting the slower electron transfer due to more effective adsorption on the electrode. The electrocatalytic reduction of CO_2 in MeCN/10% H_2O revealed catalytic waves for CO_2 reduction with E_p^c close to -1.7V and catalytic currents (i_p^c) which are about half those of the mononuclear complex, proposed to be due to steric constraints allowing strong interaction of only one nickel centre of the binuclear one on the surface. The catalytic currents increased slightly as the linking chain length increased as the stereochemical constraints were relaxed. A splitting in the catalytic peaks of the bismacrocyclic complexes that could reflect the involvement of two types of adsorbed catalyst sites. In the more sterically crowded series of complex, along with the series of linked heptaazamacrocyclic complexes much more positive redox potentials were observed due to both alkylation of the coordinated nitrogen atoms, which decreases the ligand field, and the introduction of steric barriers to axial coordination. These steric barriers prevented strong electrode interaction and led to a lower catalytic activity.

2.8.8 Macrocyclic Ligands related to Macromolecular Functions

Advances in the design of structures that exhibit combinations of simple complexes and complicated free ligands (or complexes) have appeared in the literature in recent years[350,381-385]. These assemblies, in which several subunits are linked together through noncovalent interactions, have been defined as supramolecular systems. The behaviour observed for these superstructures can be described in terms of basic concepts of supramolecular chemistry[381e], i.e. they act in molecular recognition, have supramolecular reactivity and transport, and show self-organizing tendencies with a positive cooperative display[386]. In this direction, coordinatively linked multicentre systems can be classified as supramolecular coordination compounds.

For the past 100 years, coordination chemists have produced a number of metal centered systems, many with redox activity, whose electrode potential can be conveniently modulated by synthetic modification of the coordination framework. More sophisticated systems, which are able to exchange a specified number of electrons, according to a predetermined sequence, at desired potential values, can now be prepared according to the principles of supramolecular chemistry. Moreover, the use of metal centres as structural elements allows the topology of the multi-electron redox systems to be controlled quite easily so that the redox sites can be placed in chosen positions at predetermined distances[387].

For instance, a new bifunctional super molecule (Fig. 15a) has been synthesized and its redox and CO_2 catalytic properties have been investigated[368]. Although this process induced reductive photocleavage of the supermolecule, catalytic studies show that twice the amount of CO is produced compared with the multimolecular system composed of $Ru(bpy)_3^{2+}$, pyridinium salt and Ni^{II}-cyclam.

Functionalized azacyclam complexes of Ni(II), where R is $-COCH_3$, $-COC_6H_5$ etc. have been prepared[368] and these complexes catalyze the electroreduction of CO_2 with an efficiency equivalent to that of $[Ni^{II}(cyclam)]^{2+}$, indicating that replacement of a $-CH_2$ group in the ligand backbone by an amide residue does not seriously alter the cyclam-like donor set (as far as the interaction with CO_2 is concerned) and does not disturb the catalytic process. Such a high efficiency is related to the structural features of the cyclam and azacyclam framework, i.e. a 14-membered cycle forming a 5,6,5,6 sequence of chelate rings. Even small deviations from such a geometrical arrangement cause the electrocatalytic effect to be drastically reduced or completely lost. The electron withdrawing effect of amido groups reduces the potential of the Ni^{II}/Ni^{I} couple; CO_2 is reduced to CO at a distinctly less negative potential than that observed when $Ni^{II}(cyclam)^{2+}$ is used as an electrocatalyst. Systems favouring the formation of the Ni(I) oxidation state are expected to behave as efficient electrocatalysts for CO_2 reduction. In this connection, Ni(II) complexes of some fluorinated cyclams, with Ni^{II}/Ni^{I} potentials less negative

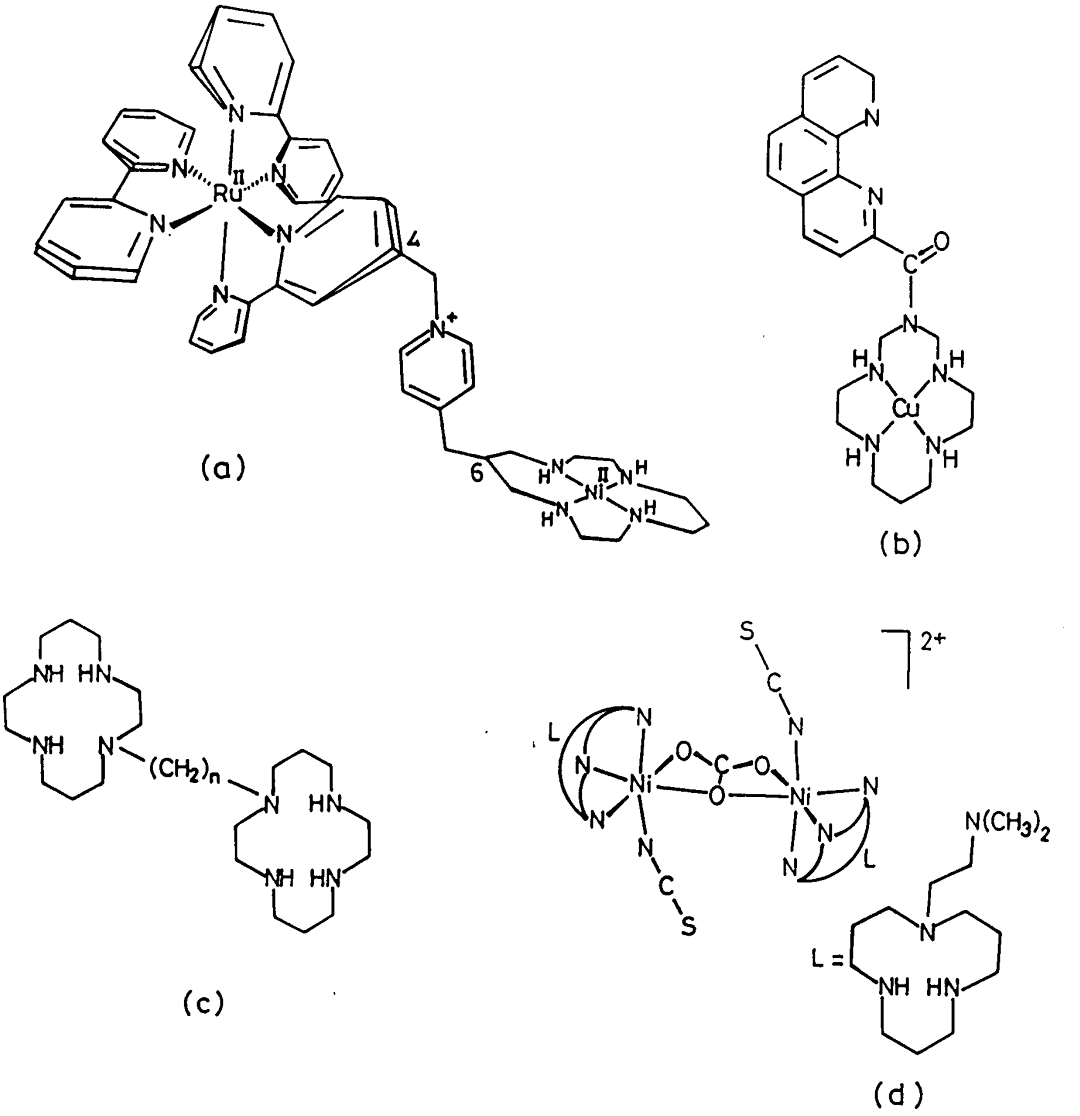


Fig. 15 Structures of macrocyclic ligands related to macromolecular functions Re (bipy) $(CO)_3^-$

than that for $Ni^{II}(cyclam)^{2+}$, work well as catalysts for CO_2 reduction[366].

The effect of attaching a metal centre to a phenanthroline backbone, as shown (Fig. 15b) in has also been investigated. These compounds, where metal complexes function as ligands, can be defined as super complexes and belong to the domain of supramolecular coordination chemistry[388]. Analogously, a pyridine subunit has been attached to a metallocyclam fragment. Covalent linking of two cyclam subunits has produced a new class of binucleating ligands (biscyclams) (Fig. 15c), which behave as ditopic receptors for transition metal ions, hosting two equivalent redox-active metal ions for example[387]. Thus the assembly of molecular components that possess specific properties is currently gaining much attention as a strategy for obtaining advanced materials. The utilization of synthetic variations and the stability of several oxidation states in these complexes has made it possible to clarify electrochemical data for these supramolecular complexes[389].

Some superstructures are able to sequester CO_2[390]. Complex shown in (Fig. 15d) has the structure of an antiferromagnetically coupled μ-carbonato-bridged bis-nickel (II) complex, which contains the pendant-arm macrocycle 1-(3-dimethylaminopropyl)-1,5,9-triaza-cyclododecane N_3. This system sequesters CO_2 from air after the addition of thiocyanate ion[390].

2 Perceptions

The large volume of work carried out in the field of CO_2 activation is difficult to summarize systematically because of the variety of approaches and experimental conditions. Plants carry out the main fixation process of CO_2 on earth. The general reaction for natural photosynthesis is:

$$CO_2 + 2\ H_2A \xrightarrow[\text{biosystem}]{h\nu} CH_2O + A_2 + H_2O$$

where 'A' is oxygen in the case of chlorophyll, and sulfur or organic acids in the case of bacteria. Under optimal conditions, the conversion of electromagnetic energy to chemical energy stored as carbohydrates occurs with 36% efficiency and requires 8 quanta/mole of reduced CO_2. The reduction of CO_2 however, is a *dark* process: CO_2 is reduced by a photo-generated reductant. Much of the input of energy and matter is spent for 'maintenance' of the system, and the fixation is only a small part in the complex process. The CO_2 fixation itself is a multistep, multielectron, complex process. Much effort and ingenuity are required for taming the process in to occurring under terrestrial conditions.

Although many fixation processes including the hydrogenation and homogeneous catalysts at high temperatures and electrochemical reductions have been proposed, one of the most essential matters in CO_2 fixation is to achieve it under an input energy as low as possible to avoid a secondary generation of CO_2. Therefore, electrochemical reactions taking place at room temperature seems to be promising. However, there are still difficult problems to be settled. e.g., a large over potential (>2.0 V on a metal electrode), low reaction rate, less valuable product (usually a C_1 compound), etc.,

The electrochemical reduction of CO_2 using various metal electrodes has been studied intensively by many workers and it has been found that the reduction products depend strongly on the electrode material. Number of studies on the electroreduction of CO_2 using various metal electrodes in aqueous and non-aqueous solutions have shown that selective (high faradaic efficiency) reduction has been performed, e.g., formic acid on Hg[107,131,391-393], Pb[17,393], In and Zn[107,140,393], CO on Ag and Au[393], methane and ethylene on Cu [142,160,393], and some hydrocarbons on various transition metals[186]. However, almost all the electrode reactions require a large overpotential for the electroreduction; they are not reversible. While several reports are available for reversible production of methanol on Ru[211], RuO_2-TiO_2 [58,59], RuO_2 [150], Ni[150], Cu[150], Mo[395] and an oxidized Cu[396], the current densities are low; their activities are not high.

Apart from the nature of electrode materials, the product distribution also depends considerably upon the reaction medium and chemisorptions of intermediates and / or products. The main concurrent reaction in aqueous solutions with CO_2 reduction is hydrogen evolution. One of the ways of discouraging hydrogen evolutions is to employ electrodes with high hydrogen over potential. An alternative approach was to separate two processes by using a Pd membrane that acts as a hydrogen reservoir[104]. Employing non-aqueous supporting electrolytes increasing the solubility of CO_2 and suppress hydrogen evolution and thereby increasing current efficiency. In addition, the occurrence of dimerization process, leading to the formation of higher C_2 products.

CO_2 has limited solubility in water (0.033 mol / dm^3 at 273 K at 1 atm)[397], which leads to mass transfer limitation for large current density electrolytes. However, CO_2 has better solubility in organic solvents. The reported solubility of CO_2 in DMSO and CH_3CN is 4 times that in water, in propylene carbonate 8 times and in DMF 20 times. Methanol is a better solvent for CO_2 than in water, particularly at low temperature. The solubility of CO_2 in methanol is ~ 5 times in water, at ambient temperatures, and 8-15 times that in water at temperature below 273 K. Due to limited solubility of CO_2 in water, it is impossible to accomplish CO_2 reduction at large current densities at 1 atm pressure. On the other hand, gas phase CO_2 can be reduced directly on gas diffusion electrodes containing electrocatalysts, such as metals and metal compounds. Thus, it is expected that CO_2 can be reduced at large current densities even at ambient pressures on a gas-diffusion electrode. Indeed, gas diffusion electrodes[398a,b] for CO_2 reduction can be operated at high current densities, i.e., 10 times higher than those achieved using metal plate electrodes. For example, Harty *et al.* investigated the electrochemical reduction of CO_2 at 1 atm using gas diffusion electrodes incorporating metal phthalocyanines, Pb, In and Sn[88,266]. They succeeded in the formation of formic acid at a faradaic efficiency of 100% on the gas diffusion electrode incorporating Pb at a current density of 115 mA/cm^2. Furuya *et al.* studied the electrochemical reduction of CO_2 using gas-diffusion electrodes containing various metal phthalocyanines and metals such as Pb, Zn, Au, Ag and Cu[398a,b,c,273]. It was shown that the partial current density of 100 mA/cm^2 for CO_2 reduction was achieved at gas-diffusion electrodes containing Pb and metal phthalocyanines.

Cook *et al.*[394] showed that methane and ethylene were produced at faradaic efficiencies of 9 and 69% respectively on Cu incorporated in a gas-diffusion electrode at a current density of 400 mA/cm^2. Moreover, they reported the formation of ethanol and propanol at faradaic efficiencies of 31 and 10% respectively on a gas-diffusion electrode incorporating $La_{1.8}Sr_{0.2}CuO_4$ at 180 mA/cm^2 [399a]. Hara et al.[247] employed gas diffusion electrode containing Pt electrocatalysts for the electroreduction of CO_2 under high-pressure conditions. The Faradaic efficiencies for CO_2 reduction reached 46% at a current density of 900 mA/cm^2.

Limitation due to reactant solubility and poor mass transport can often be over come by operating at elevated pressures. In the electrochemical reduction of CO_2 increasing mass transfer of CO_2 to the electrode is important to obtain a large reaction rate. It was proposed that a large partial pressure of CO_2 should make it possible to increase the mass transfer of CO_2 to the electrodes owing to an increase in the solubility of CO_2 in the electrolyte solution. Few reports are available on electroreduction of CO_2 under high-pressure conditions. In much of the studies[391,#99b,400,401a,b] neither identification nor quantitative analysis of the reduction products were carried out. However a series of work carried out by Hara *et al.*[174] for instance, allowed the comparison of the electroreduction of CO_2 at atmospheric pressure and at 30 atm of pressure. The electrodes were classified into four groups as follows:

(1) Ti, Nb, Ta, Mo, Mn and Al:

Hydrogen formed by reduction of water was the predominant product even at high CO_2 pressures. Increasing the CO_2 pressure did not change the product selectivity of preferential hydrogen formation.

(2) Zr, Cr, W, Fe, Co, Rn, Ir, Ni, Pd, Pt, C and Si:

Formic acid and CO form with high faradaic efficiencies at CO_2 pressure of 30 atm, where as hydrogen was the major product at pressures of 1 atm. The product selectivity changed from hydrogen to CO_2 reduction products with increase in CO_2 pressure.

(3) Ag, Au, Zn, In, Sn, Pb and Bi:

Co and formic acid were major products both at 1 atm and at 30 atm pressures.

(4) Cu:

The preferential formation of CO and HCOOH is observed, where as methane and ethylene are the major products at 1 atm CO_2. The selectivity of the CO_2 reduction products depends on the CO_2 pressure and current density.

Another technique for increasing reactant solubility is to operate in a supercritical fluid.

The electrochemical reduction is usually performed under potentio- and galvano- static condition with the products formed critically dependent on the electrodes used. These conventional galvano- / potentio- static electroreduction proceeds under the steady state conditions in which the reduction can take place sequentially from CO_2 to final products via some intermediates such as HCOOH and CO. If graphitic carbon is formed as a final product of CO_2 the 'catalytic' properties of the electrode would be masked. For example, Cu electrodes are known to loose the unique catalytic property of converting CO_2 to CH_4 and C_2H_4 because the surface is covered with carbon after a long-term electrolysis. The Cu electrode can be regarded to be apparently converted to a carbon electrode, the main product of which is hydrogen. Pulsed techniques can protect against the degradation of electrodes, due to the reduction sequence from intermediates to carbon may be interrupted by an abrupt change of the applied bias from cathodic to anodic. Pulsed electrolysis has a pronounced advantage over conventional techniques for achieving the selectivity of the reduction products when optimized with respect to cathodic bias or anodic bias and their duration.

It is well known that surface morphology at both microscopic and macroscopic levels exert a marked influence on the electrocatalytic activity of an electrode. At a microscopic level, the existence of pores, crevices, microcavities etc., favours the increase of electrodic surface area, though mass transfer, ohmic and bubble over voltages prevent the rates of electrochemical reactions from the increasing proportionally. Metallic electrodeposits allow surfaces with a variety of morphological characteristics to be obtained. Deposits with a high roughness factor and good mechanical resistance are of particular interest. These two important aspects are usually mutually exclusive, as high values of the roughness factor are mainly obtained through growth of dendrites, which have low mechanical resistance. As such coverings are unsuitable as electrocatalysts it is essential to obtain electrodeposits as a continuous metallic matrix, being highly porous and having an appropriate mechanical resistance. It is also desirable that the pores or channels increase their section in the direction towards the external surface, so as to improve the accessibility of the reactants and the current lines to the internal electrodic surface.

The application of potential periodic routines on the noble metal electrodes produces either instantaneous or permanent morphological changes depending on the characteristics of those routines[402]. Thus, the application of fast symmetrical potential perturbations on Pt electrodes in aqueous media produces perpetual changes in the morphology of the surface, that is a new defined crystallographic orientation and/or a certain surface roughness. The electrochemical responses of the resulting interfaces are generally different from those of the initial ones and the electrocatalytic activities for the processes studied may be changed accordingly exhibiting new interesting features.

Solid polymer electrolyte (spe) method can be applied to the electrochemical reduction of CO_2 in the gas phase, with out solvent, because no supporting electrolyte is required. This method thus offer an absence of catalyst poisoning owing to the solvent or electrolyte impurities and an increased mass transfer over that in solution. Therefore, metal/spe provide an added advantage in these directions.

Alternating approach for with out protonic solvents for the electroreduction of CO_2 was that construction of a hydrogenated system using a two-compartment reactor separated by a Pd sheet, which serve as a working electrode for water electrolysis to produce atomic hydrogen, a separator between the compartments, a selectively permeable membrane of atomic hydrogen and a chemical reaction field for hydrogenation. Water hydrolysis was the simple method for the production of atomic hydrogen and the electrolytic current can easily control the rate of hydrogenation, which is one of the advantages of this method. This system utilizes a rapid permeation of atomic hydrogen through the Pd sheet, which enables the hydrogenation. This system can be taken as a specific EC reaction in which the electrochemical production of atomic hydrogen and following the hydrogenation of CO_2 with permeated atomic hydrogen. Since the atomic hydrogen in this system thought to serve as a proton source and a reducing agent, CO_2 gas need not be dissolved in the solvent.

Recently, it has been found possible to produce supplies of relatively pure CO_2 at pressures of few atmospheres as an inexpensive byproduct of the electric power generation. To utilize this gas directly, one possible approach was that to make use of nanoporous catalyst supports such as activated carbon fibers, on which CO_2 [403a,b] and other gases[404,405] are known to exhibit enhanced adsorption. Within nanometer- scale pores, so-called nanospace effects exist[406] within the nanospace, e.g., the spaces between two walls, several nanometers apart, and the reaction conditions mimic high pressure[407]. Calculations of interaction potentials involving graphite micropore walls indicated enhanced potential energies[407]. The intrapore pressure of adsorbed molecule is high (over 20 Mpa). Recently, Yamamoto *et al.*[408] put together the advantages of nanospaces and gas diffusion electrodes to obtain the benefits of high-pressure conditions at ambient pressure for CO_2 reduction. Therefore, development of nanoactive materials with deposited metal catalysts may lead to realize high efficiencies.

It is essential to develop high energy, superactive metal surfaces. The term super active implies unusually active, non-equilibrium state of the metal, the characteristic feature of this state being that the metal undergoes oxidation at unusually low potentials or under unusually mild conditions. Conventional active state of metals, e.g., Pt black, are based largely on increased specific surface area, however, such deposits are not superactive as they only begin to undergo oxidation at about the same potential as the non-activated metal surface. For instance, at ca. 0.85 V (RHE) in the case of platinum in aqueous solution (as reported recently[409], super active Pt may undergo oxidation in aqueous acid solution at a much lower potential ca. 0.25 V). The basis of superactive state was discussed recently, along with its importance in electrocatalysis[409-411]. Therefore, the generation and redox behaviour of superactive state of metal surfaces is an interesting area of research and is of valuable extension for electrocatalytic processes.

In general, the direct electrochemical reduction on most metallic electrodes requires highly negative potentials, up to -2.2 V/SCE and results in a variety of products, the distribution of which critically depends on the reaction conditions such as electrode materials, solvent systems and operation parameters including current density and CO_2 concentration. This has prompted the search for suitable catalytic systems capable of mediating the electroreduction. A most interesting approach employing electrode or solution modifiers is that of homogeneous/heterogeneous catalysis.

Much work has been carried out using coordination compounds as homogeneous electrocatalysts. The compounds used as catalysts are either in solution or confined to the electrode surface. The true homogeneous electrocatalysis is that in which the catalyst, or its precursor, is regenerated by the electrode reaction, i.e., substoichiometric amounts of the catalytic active species are used with a high turnover in the second cycle coupled with the electrode reaction. Effective are those molecules that are able to transfer electrons both directly and via atom transfer. In many cases, catalytically active complexes are used in the form of a modified electrode with the catalyst attached directly to the electrode surface, using polymeric membranes incorporating the catalyst. When the polymer has the hydrophobic property, it can suppress proton reduction. The polymeric environment around the catalyst can change the catalytic activity and hence change the selectivity towards the reactant. The choice of polymer is important to construct a catalyst system with high activity for selective reduction of CO_2. The use of surface-bound catalysts is advantageous from a number of standpoints. The effective (volume) concentration of electroactive material can reach levels (ca. 0.5 M) that are simply not accessible in homogeneous solution. At such high effective concentrations, the distance between adjacent metal complex is sufficiently short that cooperativity effects are enhanced. In addition, the use of surface-immobilized electrocatalysts allows for the easy removal of the catalyst from the reaction vessel.

Metallophthalocyanines (MPCs) were employed as electrocatalysts either in solution or in immobilized form at the electrode. The PC unit is an 18π electron aromatic system that, in its common oxidation state carries two negative charges. The central metal ion may be incapable of a redox process in the usual electrochemical regime (most main group species and certain transition species such as Ni (II), Cu (II) etc.,) or may be a transition element that undergoes oxidation or reduction at potentials compared to reduction in the PC ring. The MPCs employed were: (i) CoPC > Ni PC >> FePC > CuPC > $CrPC^+$ - in which the products formed were $HCOO^-$ or CO with H_2 as the byproduct[268]. (ii) Sn, Pb and In PCs formed formic acid with H_2 as the byproduct[273]. (iii) Cu, Ga and Ti PCs formed CO and H_2 with with quantitative amounts of CH_4 (30%)[273]. (iv) Fe, Zn and Pd PCs CO was formed but in low yields compared to that of Ni and CoPCs[274]. Most unsubstituted MPC species have only very limited solubility in virtually all solvents, thereby limiting solution phase redox measurements. Ring substitution has proved to be very effective procedure for rendering these substituted MPC species soluble in a range of solvents, to an extent that, of course depend on the substituents used. Even with such species, additional solubility is conferred by axially coordinating central ions. This had led to systems that are extremely soluble in many organic solvents, for example, the tetrasulfonated phthalocyanines. Many transition metal phthalocyanines dissolve in donor solvents through an axial interaction between the metal centre and the donor solvent. This is especially to those central metal ions that strongly prefer six-coordination rather than four coordination. Thus, for example, iron (II) and cobalt (II) phthalocyanines are soluble in wide range of donor solvents, while Cu (II) PC is less soluble. Many PCs aggregate to a greater or lesser extent, both in water and organic phases. Such aggregation is influenced by pH, ionic strength, temperature, the amount of electrolyte in solution etc.[412] and thus, care must be taken in distinguishing redox potentials arising from mononuclear MPC species and from aggregated species. Aggregation is also influenced by the net charge on the MPC unit, being more predominant with positively charged species than negatively charged ones. Six-coordinate MPC species generally do not aggregate because they are kept apart by the axially bound ligands. The redox properties may be influenced by different axial ligands attached to the metal centre. This is notable especially with transition metal MPCs, since many transition metal ions prefer six-coordination and will bind a donor solvent if no other ligands are competing. Thus, redox chemistry in donor, potentially axially binding solvents can be different from that of the same MPC species in non-donor solvent such as dichloromethane.

Supporting electrolyte anions can also play an important role if they have donor characteristics. Thus, the perchlorate and hexaflurophosphate ions are usually regarded as non-donor species, although this may not be always true.

Further, the redox potentials of CoPC and its derivatives are affected by the electron donating / withdrawing property (basicity) of the complex and the CO_2 binding behaviour. The turn over number could be affected by the electronic property of the catalyst. The substitution of electron donating groups such as BuO- facilitate the coordination of CO_2 as well as the electron transfer from the complex to the coordinated CO_2 molecule. For instance, Abe *et al.*[277] achieved selective CO_2 electroreduction by employing (CoPC $(BuO)_8$).

Later they[288] have studied the role of electron withdrawing groups such as CN^- by using $(CoPC(CN)_8)$. The redox reaction proceeds at more positive potential than that of non-substituted CoPC. The electronic donating property of this system is weak but the observation was attributed to the higher fraction of electroactive species on the electrode surface. The rate determining step is different for $(CoPC(CN)_8)$ and CoPC. Thus, electronic property would be a dominant factor in the catalytic mechanism and leads to different rate determining step in the catalytic cycle. Thus, in general, the choice of ligand strongly influences the electrochemical properties. Electron withdrawing groups lead to a positive shift of redox potentials, electron-donating groups to a negative shift. The redox chemistry of MPCs is extensively dealt with elsewhere[414].

Porphyrins are considered as related to PCs, for there are quite close similarities in the gross behaviour of both series of complexes. In general, the lower basicity of the PCs relative to the porphyrins result in the greater stabilization of the lower oxidation states in the former. That is, the lower oxidation states of central transition metal ions are more readily accessible in the PCs than in the porphyrin series. Metalloporphyrins are active catalysts in the electroreduction of CO_2 to CO in aqueous and non aqueous media and the example include Co, Fe, Cu metalloporphyrins and substituted porphyrins of Pd and Ag. These complexes seem to decompose in long-term electrolysis conditions, though they markedly decrease the over voltage for reducing CO_2. The product distribution mainly depends on the metal and solvent used.

Substitution of aza groups has greater impact on the structure of the reaction centre of porphyrin ligands and to a large extent determines the structure and properties of PCs. It decreases the dimensions of the coordination cavity and increases the acidity of the N-H bonds, creating conditions for the formation of strong intramolecular hydrogen bonds in tetraaza porphyrins and PCs. The synthesis and redox properties of porphyrins are discussed elsewhere[413].

An alternative method for immobilizing catalysts on to electrode surface has been through the use of complexes containing polymerizable ligand. For example, vinyl substituted ligands, i.e., electroploymerization of $[Re(CO)_3$ (v-PPY) Cl] (v-PPY is 4- vinyl –4’- methyl –2,2’- bipyridine) give rise to the formation of redox active polymeric films, which can reduce CO_2 to CO electrocatalytically[415].

Metal complexes with unsymmetrical chelating rings may also provide sites for activation of CO_2 by dechelation in the electrochemical reduction of CO_2. For example, dmbbbpy (2,2’- bis (1-methylbenzimidazol-2-yl)-4,4’-bipyridine chelating into a $Ru(bpy)_2$ moiety, to create more reaction site by opening the chelating ring and to accumulate electrons in to the ligand required in the reduction of CO_2.

The addition of Lewis acids and Bronsted acids to the electrocatalytic systems such as iron porphyrin seems to enhance the catalytic current and life time of the catalyst. The role of acid is to pull off the electrons out of the substrate (CO_2) by facilitating the cleavage of one of the two C-O bonds resulting in the formation of CO and H_2O. Besides, enhancing the rate of catalysis, it appears that the presence of proton sources, in the electrolyte can also affect the product distribution.

The tuning of the redox properties of the catalytic site may lead to different electrochemical behaviour of the system. For instance, Nallas *et al.*[317] employed a trimetallic system, in which two remote Ru centres serve to tune the redox properties of the central catalytically active $Ir^{III}(BL)_2Cl_2$ core [BL = dpq or dpb]. In this system, the redox properties of the catalytic site can be altered through remote metal coordination and variation without a change in the coordination environment of the catalytic iridium site.

Organometallic complexes have also been employed as possible electrocatalysts. Complexes containing carbonyl and 2,2’-bipyridyl (bpy) ligands have been studied as the latter offers π^* orbitals close in energy to the antibonding d orbitals of the later transition metal elements, so allowing the complex to act as an electron sink. Thus, [Re (bpy) (CO) Cl] can convert CO_2 to CO with 95% current efficiency at –1.5 V in mixed protic / aprotic media, without appreciable loss of activity over 300 cycles[300], though the mechanism is not fully understood[299,322].

Many of the tetraaza macrocyclic complexes synthesized in the past 30 years displayed structural analogies with metalloporphyrins. In particular, square planar geometries are favoured leaving the axial sites free with the possibility of coordinating additional ligands on the axial positions. However, the electronic properties of porphyrins are very different from that of synthetic tetraazamacrocyclic ligands. In 1970s Busch *et al.*[416] synthesized and investigated series of nickel and cobalt aza macrocycles with varying degrees of unsaturation, ring-size and ring substituents and their influence on redox behaviour. Adam *et al.*[417] carried out similar studies for nickel tetraazamacrocycles. The result of such systematic studies establishes that the electronic and structural features that promote and retard their electron transfer reactions.

The understanding of CO_2 binding and activation by transition metal complexes has considerably increased. Any type of binding known to date to result in coordination compounds containing CO_2 as a ligand leads to a net electron transfer to the LUMO of the CO_2 and thus lead to it's activation. Accordingly, coordinated CO_2 undergoes reactions that are impossible for free CO_2 and complexes containing CO_2 ligand as in stable complexes are most likely involved in C-O cleavage reactions. Weak interactions between the metal centre and the lone pairs of one oxygen of CO_2, similar to those found in gas phase complexes of 'naked' metal ions and CO_2, are often sufficient to support the insertion process by pre-organization of CO_2 molecule. Most of the synthetically useful transition- metal- mediated transformations of CO_2 known to date seem to follow this general pathway. The optimization of existing processes and the search for new reactions involving CO_2 as a environmentally friendly and economically feasible source of carbon can only be successful if we understand the underlying principles of CO_2 activation. The effective 'activation' of CO_2 by transition metal compounds is still a goal that is hard to reach and remains as exciting research area in organometallic chemistry.

The basic aims in using metal complexes that structurally or functionally mimic biomolecules include:

- Their coordinating ability is suitably and sterically altered to accommodate the facile reduction of $CO_{2.}$
- The metal complexes could be manipulated either in terms of redox potentials or by way of mediated energy levels so as to facilitated reduction.
- Since these complexes dissociate, disproportionate, alter their coordination sphere as well as their oxidation states, they are amenable for development of cyclic processes for the reduction of CO_2.
- A variety of products, especially various reduced products could be obtained depending on the redox potential, steric and coordinative geometry for simultaneous activation of hydrogen containing species.

These systems have to be designed and tailored suitably in such a way that they will be able to coordinate, couple and generate reduced species within the coordination sphere without undergoing any substitutive degradation or deactivation.

The future electrocatalysis lies not so much in the improvement of electrochemical methods – it lies essentially on the side of design of new catalysts. The design of such a catalyst is not an easy task, as at the same time the compound must meet some electrochemical requirements such as appropriate reduction potentials of all steps, fast electron transfer to the electrode, easy intramolecular electron transfer, stability of intermediates and possibly, electrochemical reactivity of intermediate with the substrate attached to the catalyst. The search for such catalysts will attract continuous attention not only of electrochemists but also of synthetic molecular engineers.

3 Concusion and Outook

Unfortunately, the predominant product of CO_2 reduction so far has been only C_1 compounds (CO, HCOOH, CH_4 or MeOH). A desirable target should be a C_n hydrocarbon or C_n alcohol, with n exceeding at least two. Even the ultimate C_1 species, viz., CH_4 requires 8 electrons, requiring a multielectron reducing agent for a single-step process. The challenge facing a facile route towards a C_n product is thus obvious. In spite of the vast amount of work already carried out, the search for a strategy to reduce CO_2 to obtain a desired product by a route with minimum energy / cost input has a long way to go. Those engaged in this search should perhaps reconcile themselves to a multistep reduction process as inevitable.

A Few Additional Features

- The reducing agent is photo / electro generated.
- The reduction potential of the source of reducer should be least cathodic.
- Water is necessarily a solvent if the catalyst is a metal complex, and hydrogen reduction, a parallel process. This also means low CO_2 solubility and low current.
- The catalyzed process could ensure product selectivity and high efficiency by using polymer-modified electrodes.
- Direct uncatalyzed reduction on the electrode may use non-aqueous solvents like MeOH and low temperatures to increase solubility and hence high current, but so far only at a high over voltage (ca. –2.0V).
- A high CO_2 pressure also ensures high current.
- For most systems reported, kinetic data available to discern the operating mechanisms are insufficient.

- Basic research emphasizing mechanistic aspects of this chemistry is needed.
- The search for new catalysts and processes must rely on a better understanding of the mechanisms of those already discovered.

Investigation of catalytic activation of CO_2 recognizes a variety of sub-disciplines – homogeneous catalysis, heterogeneous catalysis, electrocatalysis, photoelectrocatalysis, as they were dictated both by the aim of the research (e.g., understanding photosynthesis, producing useful chemicals, energy storage) and by the training of the investigator.

Nature is a good teacher, and many catalytic systems try to mimic natural processes. A symbiosis exists between technological and biological processes, the former helping to understand and simulate the later, and the later providing the guidelines for designing new catalysts.

Abbreviations

bpm	2,2'-bipyrimidine
bpy	2,2'-bipyridyl
CH_3CN	acetonitrile
CRH	2,12dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17), 13,15-triene
cyclam	1,4,8,11-tetraazacyclotetradecane
dmbipy	4,4'-dimethyl-2,2'-bipyridine
DMF	N,N'-dimethylformamide
DMSO	N,N'-dimethylsulfoxide
dpp	2,3'-bis(2-pyridyl)pyrazine
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2- bis(diphenylphosphino)methane
dppp	1,2- bis(diphenylphosphino)propane
dpq	2,3'-bis(2-pyridyl)quinoxaline
L	neutral or anionic ligand
MPC	metallophthalocyanine
PAn	polyaniline
PB	Prussian blue
Pc	phthalocyanine
PC	propylene carbonate
PVP	polyvinylpyridine
py	pyrene
pyra	pyrazole
qtpy	2,2': 6',2": 6",2'"-quaterpyridine
TBAP	tetrabutylammonium perchlorate
TEAP	tetraethylammonium perchlorate
THF	tetrahydrofuran
TMC	tetra-N-methylcyclam
TPP	tetraphenylporphyrine
vitpy	4'-vinyl-2,2': 6',2"-terpyridine

Notations

CB	conduction band
CV	cyclic voltammetry
CT	charge transfer
EPR	electron paramagnetic resonance
HER	hydrogen evolution reaction
HMDE	hanging mercury drop electrode
^{1}NMR	proton magnetic resonance
HOMO	highest occupied molecular orbital
IR	infrared
LUMO	lowest occupied molecular orbital
NHE	normal hydrogen electrode
rf	turnover frequency
SCE	saturated calomel electrode
TOF	turnover frequency, TON per hour
TON	turnover number, moles product per mole of catalyst
UV	ultraviolet
VB	valence band

Acknowledgement

We gratefully acknowledge the Council of Scientific and Industrial Research (CSIR), New Delhi, for the award of a Research Associateship to the author (MAS).

References

1 *Carbondioxide Chemistry, Environmental Issues* (Eds J Paul and C - M Pradier) Royal Society of Chemistry London (1994)

2 E T Sundquist *Science* **259** (1993) 934

3 P S Zurer *Chem Engg News* **69(13)** (1991) 7

4 U Siegenthaler and J L Sarmiento *Nature* **365** (1993) 119

5 John and M Gribbin *New Scientist* **92** (1996) 1

6 K Weissermel and H-J Arpe *Industrielle Organische Chemie* (3d Edition) VCH Weinheim (1988)

7 *Organic and Biorganic Chemistry of* CO_2 (Eds S Inoue and N Yamazaki) Wiley New York (1982)

8 A Beher *Carbon Dioxide Activation by Metal Complexes* VCH Weinheim (1988)

9 *Catalytic Activation of Carbon Dioxide* (ACS Symp Ser) (1988) 363

10 *Enzymatic and Model Carboxylation and Reduction Reaction for Carbon Dixoide Utilization* (NATO ASF Ser C 314 (1990)

11 *Electrochemical and Electrocatalytic Reaction of Carbon Dioxide* (Eds B P Sullivan, K Krist and H E Guard) Elsevier Amsterdam (1993)

12 M M Halmann *Chemical Fixation of Carbon Dixoide* CRC Boca Raton (1993)

13 D Walther *Coord Chem Rev* **79** (1987) 135

14 *Römpp Chemie Lexikon* (Eds J Falbe and M Regitz) 9th edition Thieme Stuttgart (1990) 2277

15 *Handbook of Chemistry and Physics* (Eds R C Weast) CRC 65th Ed Boca Raton (1984)

16 Kirk - Othmer *Enzyclopedia of Chemical Technology* Wiley New York **5** (4th ed) (1993) 35

17 F M Field and J L Fracklin *Electron Impact Phenomena and the Properties of Gaseous Ions* Academic Press New York (1958)

18 F A Cotton *Chemical Applications of Group Theory* Wiley Eastern New Delhi 2nd Edn (1976)

19 J W Rabalais, J M McDonald, V Sherr and S P M McGlynn *Chem Rev* **71** (1971) 73

20 K S Sindhu, I G Csizmadia, O P Strausz and H F Guinning *J Am Chem Soc* **88** (1988) 2412

21 L Pauling *The Nature of the Chemical Bond*, Cornell University Press Ithaca New York (1969) pp 268

22 I L Karle and J Karle *J Chem Phys* **17** (1949) 1057

23 H E Thennecke and R S Drago *J Am Chem Soc* **90** (1968) 5112

24 D D Wagman, W H Evans, V B Parker, R H Schumm, I Halow, S M Bailey, K L Chburney and R L Nuttall *J Phys Chem* Ref Data 11 Suppl 2 (1982)

25 K D Jordon *J Phys Chem* **88** (1984) 2459

26 B E Douglas, D H McDaniel, J J Alexander *Concepts and Models of Inorganic Chemistry* John Wiley 2nd Ed (1983)

27 R Eisenberg, D E Hendriksen *Adv Catal* **28** (1979) 79

28 M E Vol'pin, I S Kolomnikov and T S Lobeera *Izv Akad Nauk SSSR Ser Khim* (1969) 20

29 P W Jolly, K Jonas, C Krüger and Y-H Tsay *J Organomet Chem* **33** (1971) 109

30 N W Alcock *Bonding and Structure* Ellis Herwood London (1990)

31 K D Hartmann and I C Isatune *J Chem Phys* **44** (1966) 1913

32 D H Gibson *Chem Rev* **96** (1996) 2063

33 K K Pandey *Coord Chem Rev* **140** (1995) 37

34 A W Boyd and C Willeis *Int J Radiat Phys Chem* **8(1-2)** (1976) 71

35 N Getoff, G Scholes and J Weiss *Tetrahedron Lett* (1960) 17

36 A Voss *Brennst - Waerme - Kraft* **42(10)** (1990) 579

37 T T Kobler, P Schaumann and A Voss *Atom Wirsth Atomtech* **35(10)** (1990) 484

38 V S Komissararo, V F Krasnoshtanov and V L - B Khodulev *Vapr Atom Naukii Tekhn Atom - Vodorod Energy Moskvu* **2** (1997) 48

39 E L Quinn and C L Jones *Carbon Dioxide* Reinhold New York (1936)

40 C E Bamberger and P R Robinson *Inorg Chim Acta* **42** (1980) 133

41 J M Lehn and R Ziessel *Proc Natl Acad Sci* U S A **79** (1982) 701

42 N Getoff, *Z Natureforsch* **B 17** (1962) 87

43 C Amatore and J M Saveant *J Am Chem Soc* **102** (1981) 5021

44 H S Jee, N Nishio and S Nagai *J Ferment Technol* **66** (1988) 235

45 H S Jee, N Nishio and S Nagai *Biotechnol Lett* **10** (1988) 243

46 I Willner, D Mandler and J Riklin *J Chem Soc Chem Commun* (1986) 1022

47 D Mandler and I Willner *J Chem Soc Perkin Trans* **2** (1988) 997

48 I Taniguchi B Aurian - Blajeni and H O'M Bockris *Electrochim Acta* **29** (1984) 923

49 M Ulman, B Aurian - Blejni and Halmann *CHEMTECH* 235 (1984)

50 K Sugimura, S Kuwabata and H Yoneyama *J Am Chem Soc* **111** (1989) 2361

51 B A Parkinson and P F Weaver *Nature* **309** (1984) 149

52 M E Royer, *C R Acad Sci* **70** (1870) 731

53 W Leitner *Angew Chem Int Ed Engl* **34** (1995) 2207

54 M Aulice Scibioh and V R Vijayaraghavan *J Sci Ind Res* **57** (1998) 111

55 E Lamy, L Nadjo and J M Savéant *J Electroanal Chem* **78** (1977) 403

56 A J Bard *Encyclopedia of Electrochemistry of the Elements* Dekker New York **7** (1976)

57 M M Halmann and M Steinberg *Greenhouse Gas Carbon Dioxide Mitigation Science and Technology* Lewis Publishers Boca Raton FL (1997)

58 A Bandi and H M Kuhne, *J Electrochem Soc* **139** (1992) 1605

59 A Bandi *J Electrochem Soc* **137** (1990) 2157

60 V S Bagotzku and N V Osetrova *Russ J Electrochem* **31(5)** (1995) 409

61 W M Latimer *Oxidation Potentials* Prentice Hall Edgewood Cliffs New Jersey (1952)

62 *Tables of Chemical Thermodynamic Properties National Bureau of Standards* Washington D C (1982)

63 W H Koppenol and J D Rush *J Phys Chem* **91** (1987) 4427

64 H A Schwarz and R W Doson *J Phys Chem* **93** (1989) 409

65 G P Laroft and R W Fessenden *J Phys Chem* **77** (1973) 1283

66 G V Buxton and R M Sellers *J Chem Soc Faraday Trans* **69** (1973) 555

67 W Paik, T N Anderson and H Eyring *J Phys Chem* **46** (1972) 3278

68 I Willner, R Maidan, D Mandler, H Dürr, G Dörr and K Zengerle *J Am Chem Soc* **109** (1987) 6080

69 M Halmann and K Zuckerman *J Electronal Chem Interfacial Electrochem* **235** (1987) 369

70 J Jordan and P T Smith *Proc Chem Soc* (1960) 246

71 L V Haynes and D T Sawyer *Anal Chem* **39** (1969) 332

72 W Paik, T N Anderson and H Eyring *Electrochim Acta* **14** (1969) 1217

73 J Ryu, T N Anderson and H Eyring *J Phy Chem* **76** (1972) 3278

74 A W B Aylmer Kelly, A Bewick, P R Cantrill and A M Texford *Discussions Faraday Soc* **56** (1973) 96

75 J H Lansford and J P Jayne *J Phy Chem* **69** (1965) 2182

76 D W Overnall and D H Whiffen *Mol Phys* **4** (1961) 135

77 S Wazonek and A Gundersen *J Electrochem Soc* **111** (1964) 324

78 D J Schiffrin *Discussions Faraday Soc* **56** (1973) 75

79 A Bewick and G P Greener *Tetrahedron Lett* **53** (1969) 4623

80 A Bewick and G P Greener, *Tetrahedron Lett* **5** (1970) 391

81 U Kaiser and E Heitz *Bar Bunsenges Phys Chem* **77** (1973) 818

82 B R Eggins and J McNeill *J Electroanal Chem* **148** (1983) 17

83 C M Bolinger, N Story, P Sullivan and T J Meyer *Inorg Chem* **27** (1988) 4582

84 H Stephen and T Stephen, *Solubilities of Inorganic and Organic Compounds* Macmillan New York (1963)

85 T Yammamoto *Bull Inst Phys Res* (Tokyo) **7** (1922) 999

86 H C Hurrell, A - L Mogstad, D A Usifer, K T Potts and H D Abruna *Inorg Chem* **28** (1989) 1080

87 B Aurion - Blajeni, M Halmann and J Masnassen *Solar Energy Mater* **8** (1983) 425

88 M N Mahmood, D Masheder and C J Harty *J Appl Electrochem* **17** (1987) 1159

89 D Masheder and K P J Williams, *J Raman Spectrosc*, **18** (1987) 387

90 E R Brown and J R Sandifer *Physical Methods of Chemistry* (Ed R W Rossiter and J F Hamilton) Wiley New York **2(4)** (1986) 273

91 O J Murphy and S Srinivasan *Electrochemistry in Transition* Ch 22, B A Blajeni Electrochemical Reduction of CO_2 Plenum Press New York

92 A Seidell and W F Linke *Solubilities* Van Nostrand, New York (Supplment to 3rd edition) (1949)

93 A Seidell *Solubilities of Inorganic and Metal Organic Substances* Van Nostrand New York **1** (1940)

94 K Ogura and H Uchida *J Chem Soc Dalton Trans* (1987) 1377

95 K Ogura and I Yoshida *J Mol Catalysis* **34** (1986) 676

96 A Murata and Y Hori *Bull Chem Soc Jpn* **64** (1991) 123

97 I Taniguehi, B A Blajeni and J O' M Bockris *J Electroanal Chem* **157** (1983) 179

98 J O' M Bockris and J C Wass *J Electrochem Soc* **136** (1989) 2521

99 I Taniguchi, B A Blajeni and J O' M Bockris *J Electroanal Chem* **161** (1983) 385

100 H Yoneyama, K Sugimara and S Kuwabata *J Electroanal Chem Interfacial Electrochem* **249** (1988) 143

101 Y Hori, A Murata, R Takahashi and S Suzuki *J Chem Soc Chem Commun* (1988) 17

102 D J Pearce and D Pletcher *J Electroanal Chem* **197** (1986) 317

103 T Saeki, K Hashimoto, N Kumura, K Omata and A Fujishima *J Electroanal Chem* **390** (1995) 77

104 D P Summers and K W Frese *Catalytic Activation of CO_2* (Ed William M Ayers) ACS Symposium Series 363 American Chemical Society Washington D C (1988)

105 B Aurian - Blajeni *Electrochmistry in Transition* (Ed O J Murphy, S Srinivasan and B E Conway) Plenum Press New York (1992)

106 K Ito, Sh Ikeda and H Noda *Sol Eng Congr Proc Bienn Congr Int Sol Energy Soc* (Ed M E Ardan and M A Susan) Bergamon Oxford **1**(2) (1992) pp 884; *Chem Abst* **118** (1993) 13205a

107 Sh Ikeda, T Takagi and K Ito *Bull Chem Soc Jpn* **60** (1987) 2517

108 (a) L Oniciu, M Jitaru and G Bocea *Electrocataliza* (Ed Stiintifica) Bucharest (1991) pp 305; (b) M Jitaru, D A Lowy, M Toma, B C Toma and L Oniciu *J Appl Electrochem* **27** (1997) 875

109 H Lund and M M Baizer *Organic Electrochemistry* Marcel Dekker New York (1991) pp 20

110 V S Bagotskii and Yu Vasiliev *J Electroanal Chem Interfacial Electro Chem* **271** (1985) 189

111 V V Kesarev and V S Fedortsov *Zh Briklad Khim* **42** (1969) 707

112 K Ito and T Murata *Bull Nagoya Ind Technol* **271** (1975) 369

113 K Ito and S Ikeda *Bull Chem Soc Jpn* (1987) 2517

114 H Kita *Electrochemistry* (Ed H Bloon and F Gutman) Plenum Press New York (1975) 131

115 L Oniciu, D A Lowy, M Jitaru and B C Toma *Studies Univ Babes - Bolyai Chemia* **33** (1988) 87

116 L Oniciu, D A Lowy and M Jitaru *Bull Electrochem* **4** (1988) 1041

117 L Oniciu, M Jitaru, D A Lawy and B C Toma *Extended Abstracts of the 39th Meetings of ISE* Glasgow (1988)

118 L Oniciu, M Jitaru and I A Silberg *Rev Roum Chim* **34** (1989) 537

119 M Jitaru, B C Toma and M Toma *Extended Abstracts of the Academic Days* 21-23 Apr 42 Timisora (1993)

120 M Jitaru, B C Toma and M Toma *Extended Abstracts of the 6th Conference of Physical Chemistry* 23-25 Sept Bucharest (1992) 149

121 M Spichiger - Ulmann and J Augustynki *J Chem Soc Faraday Trans* **181** (1985) 713

122 M Spichiger - Ulmann and J Augustynski *Nouv J Chem* **10** (1986) 487

123 Y Hori, K Kikuki, S Suzuki and A Murata *Chem Lett* (1986) 893

124 N V Osetrova, Yu B Vassilev and V S Bagotsky *Electrosintez Monomerov* (Ed V V Tomilov) Izd Nauka, Moscow (1980) pp 220

125 F Solymosi, A Erdöhelyi and M Kocsis *J Catal* **65** (1980) 428

126 F Solymosi, A Erdöhelyi and T Bánsági *J Catal* **68** (1981) 371

127 H Noda, S Ikeda, Y Ora and K Ito *Chem Lett* 289 (189)

128 H Noda, Sh Ikeda, Y Ora, K Imai, M Mreda and K Ito *Bull Chem Jpn* **63** (1990) 459

129 K Ito, Sh Ikeda, N Yamauchi, T Iida and T Takagi *Bull Chem Soc Jpn* **58** (1985) 3027

130 M Chandrasekaran, T Raju, and V Krishna *Bull Electrochem* **8** (1992) 124

131 K S Udupa, G S Subramanian and H V K Udupa *Electrochim Acta* **16** (1971) 1593

132 M E Royer *Compt Rend* **70** (1870) 731

133 A Coehn and S Jahn *Ber Dtsch Chem Ges* **39** (1904) 2836

134 R Ehrenfeld *Ber Dtsch Chem Ges* **38** (1905) 4138

135 F Fischer and O Prziza *Ber Dtsch Chem Ges* **47** (1914) 256

136 M Rabinowitsch and A Maschowetz *Z Elektrochem* **36** (1930) 846

137 A Katoh, M Shibata and M Watanabe *Denki Kagaku* **61** (1993) 805

138 M Watanabe, M Shibata, A Katoh and H Uchida *Proc Electrochem Soc* (Proceedings of the Symposium of Environmental Aspects of Electrochemistry and Photoelectrochemistry) (1993) 93-18

139 S Ishimaru, R Shiratsuchi and G Nogami *J Electrochem Soc* **147(5)** (2000) 1864

140 S Kapusta, and N Hackerman, *J Electrochem Soc* **130** (1983) 607

141 S Komatsu, T Yanagihara, Y Hiraga, M Tanaka and A Kunugi *Denki Kagaku* **63**, (1995) 217

142 Y Hori, K Kikuchi, A Murata and S Suzuki *Chem Lett* (1985) 897

143 Y Hori, K Kikuchi and S Suzuki *Chem Lett* (1985) 1695

144 Y Hori *Proc Electrochem Soc* 93-18 (Proceedings of the Symposium on Environmental Aspects of Electrochemistry and Photoelectrochemistry) (1993) 1

145 A Naitoh, K Ohta and T Mizuno *Chem Express* **8** (1993) 145; *Chemical Abstracts* **118** (1993) 156698z

146 A Naitoh, K Ohta, T Mizuno, H Yoshida, M Sakai and H Noda *Electrochim Acta* **38** (1993) 2177

147 R Shiratsuchi, Y Aikoh and G Nogami *J Electrochem Soc* **140** (1993) 3479

148 A Fujishima and K Hasimoto *Photochemical and Photoelectro Chemical Conversion and Storage of Solar Energy* Proceedings of the 8th Conference (Ed L W Tian) (1992) Int Acad Publ Beijing (1993) 307

149 K Hwang, M Nam, D J Park and H Kim *Proc Electrochem Soc* 93-11 (Proceedings of the fifth International Symposium on Redox Mechanisms and Interfacial Properties of Molecules of Biological Importance) (1993) 248

150 Y Nakato *Kagaku to Kagyo (Tokyo)* **46** (1993) 1417; *Chem Abst* **120** (1994) 146872d

151 Y Nakato *Proc Electrochem Soc* 93-18 (Proceedings of the Symposium on Environmental Aspects of Electrochemistry and Photoelectrochemistry) (1993) 78

152 K Ohkawa, K Hashimoto, A Fujishima, Y Noguchi and S Nakayama *J Electroanal Chem* **345** (1993) 445

153 K Ohkawa, Y Noguchi, S Nakayama, K Hashimoto and A Fujishima *J Electroanal Chem* **369** (1994) 247

154 K Hashimoto, K Ohkawa and A Fujishima *Proc Electrochem Soc* 93-18 (Proceedings of the Symposium on Environmental Aspects of Electrochemistry and Photoelectrochejistry) (1993) 22

155 B Jermann and J Augustynski *Electrochim Acta* **39** (1994) 1891

156 S Wasmus, E Cattaneo and W Vielstich *Electrochim Acta* **35** (1990) 771

157 J J Kim, D P Summers and K W Frese Jr *Extended Abstracts of the 172nd Meeting of the Electrochem Soc* 18-23 Oct (1987) 828

158 Sh Ikeda, S Amakusa, H Noda, Y Saito and K Ito *Extended Abstract of the 172nd Meetings of the Electro Chem Soc* 18-23, Oct (1987) 829

159 R L Cook, R C MacDuff and A F Sammels *J Electrochem Soc* **134** (1987) 1873

160 Idem *ibid* **134** (1987) 2375

161 Idem *ibid* **135** (1988) 1320

162 Idem *ibid* **135** (1988) 1470

163 Idem *ibid* **136** (1989) 1982

164 Idem *ibid* **135** (1989) 3069

165 R L Cook, R C MacDuff U S Patent US 4 879167 (1990)

166 A Katoh, H Uchida, M Shibata and M Watanabe *J Electrochem Soc* **141(8)** (194) 2054

167 K Hara, A Tsuento, A Kudo and T Sakata *J Electrochem Soc* **141(8)** (1994) 2097

168 J Li and G Prentice *J Electrochem Soc* **144(12)** (1997) 4284

169 S Kaneco, K Iiba, N - Hiei, K Ohta, T Mizuno and T Suzuki *Electrochim Acta* **44** (1999) 4701

170 S Kaneco, K Iba, S Suzuki, K Ohta, T Mizuno *J Phy Chem B* **103** (1999) 7456

171 Sh Ikeda, T Ito, K Azuma, K Ito and H Noda *Denki Kagaku* **63** (1995) 303

172 S Komatsu, M Tanaka, A Okumura and A Kungi *Electrochem Acta* **40** (1995) 745

173 K Watanabe, U Nagashima and H Hosoya *Chem Phys Lett* **209** (1993) 109

174 K Hara, A Kudo and T Sakata *J Electroanal Chem* **391** (1995) 141

175 R Hernandez, J Margez, O Marquez, M Choy Martinez, C Ovalles, J J Garcia and B Schariffer *ibid* 169; *Chem Abstr* **119** (1993) 82087W

176 M Jitaru, L Oniciu, M Toma, B C Toma and D A Lowy *Studia Univ Babes - Bolyai Chemistry* (1998)

177 L Oniciu, D A Lowy, I A Silberg, M Jitaru, F Ciomos, O H Oprea, B C Toma and M Toma *Rev Roum Chim* **35** (1990) 859

178 L Oniciu, I A Silberg and F Ciomos *Rev Chem* (Bucharest) **36** 406 (1985) 406

179 Idem *ibid* **36** (1985) 481

180 Idem *ibid* **36** (1985) 628

181 L Oniciu, D A Lowy M Jitaru and B C Toma *Extended Abstract of the XXIst International Conference on Solution Chemistry* Ottawa Canada 5-10, Aug (1990)

182 L Oniciu, D A Lowy and M Jikaru *Extended Abstracts of the XXth International Conference on Solution Chemistry*', The Hebrew University Jerusalem (1989)

183 G Z Kyriacou and A K Anagnostopoulos *J Appl Electrochem* **23** (1993) 483

184 M Todoroki, K Hara, A Kudo and T Sakata *J Appl Electroanal Chem* **394** (1995) 199

185 H Noda, Sh Ikeda, Y Oda, K Imai, M Maeda and K Ito *Bull Chem Soc Jpn* **63** (1990) 2459

186 M Azuma, K Hashimoto, M Watanabe and T Sakato *J Electroanal Chem* **294** (1990) 299

187 Y Hori, A Murata, K Kikuchi and S Suzuki *J Chem Soc Chem Commun* (1987) 728

188 B R Eggins, E M Brown, C A McNeiu and Y Grimshaw *Tetrahedron Lett* **29** (1988) 945

189 A Bewick and G P Greener *ibid* (1969) 4623

190 A Bewick and G P Greener *ibid* (1970) 391

191 F Wolf and J Rottlin *Z Chem* **17** (1970) 37

192 A T Kuhn *Brit Chem Eng* **17** (1971) 39

193 V Von Kaiser and E Heitz Ber Bunsen - Ges *Phys Chem* **77** (1978) 818

194 W M Ayers *Spec Publ - R Soc* (*Carbondioxide Chemistry Environmental Chemistry* (1994) 365

195 K W Frese *Electrochemical and Electrocatalytic Reactions of Carbondioxide* (Eds B P Sullivan, K Krist and H E Guard) Elsevier Amsterdam London New York Tokyo (1993) 148

196 R Kostecki and J Augustynski *ibid* **98** (1994) 1510

197 R Shiratsuchi and G Nagami *J Electrochem Soc* **143(2)** (1996) 582

198 S Kaneco, K Iiba, K Ohta, T Mizuno and A Saji *Electrochim Acta* **44** (1998) 573

199 Ch J Chang, Ch - Y Chen and H - Ch Lin *J Chem Eng Data* **40** (199) 850

200 J C Gressin, D Michelet, L Nadjo and J - M Saveant *Nouveau J Chim* **3** (1979) 545

201 C Amatore and J - M Saveant *J Am Chem Soc* **103** (1981) 5021

202 L V Haynes and D T Sawyer *Anal Chem* **39** (1967) 332

203 A Gannao, Abdirisak A Isse, Maia - Gabriella Severin, E Vianello, I Bhugan and J M Saveant *J Chem Soc Faraday Trans* **92(20)** (1996) 3963

204 Yu B Vassilieu, V S Bagotsky, N V Osetrova, O A Kabzova and N A Mayorova *J Electroanal Chem* **189** (1985) 295

205 K Ito, Sh Ikeda, T Lida and A Nomura *Denki Kagaku* **50** (1982) 463

206 K W Frese Jr *Electrochemical and Electrocatalytic Reactions of CO_2* (Eds B P Sullivan, K Krist and H E Guard) Elsevier Amsterdam London New York Tokyo (1993) 152

207 T Mizuno, A Naitoh and K Ohta *J Electroanal Chem* **391** (1995) 199

208 T Saeki, K Hashimoto, N Kimura, K Omata and A Fujishima *Chem Lett* (1995) 361

209 E Brunner, W Hültenschmidt and G Schichlträrle *J Chem Thermodyn* **19** (1987) 273

210 J Giner *Electrochim Acta* **8** (1963) 857

211 K W Frese Jr and S Leach *J Electrochem Soc* **132** (1985) 259

212 K W Frese Jr and D P Summers *Electrochemical Surface Science* (ACS Symposium Series 378) (Ed W M Ayers) ACS Washington DC (1988)

213 D P Summers and K W Frese *J Electrochem Soc* **35** (1988) 264

214 S Chao, C J Stadler, D P Summers and M S Wrighton *J Am Chem Soc* **106** (1984) 2723

215 J P Popic, M L Auramov Ivi and N B Vukovi *J Electroanal Chem* **421** (1997) 105

216 W M Ayers and M Failey *J Am Chem Soc* **110** (1988) 147

217 M Grden, A Paruszewska and A Czerwinski *J Electroanal Chem* **502 (1-2)** (2001) 91

218 N Inuzuka *Jpn Kokai Tokkyo Koho* JP 04 314 881 6 Nov (1992) *Chem Abst* **120** (1994) 333692g

219 C U Maier, A Bandi and M Specht *J Electrochem Soc* **141** (1994) L4-L6

220 J Schwarz, C U Maier and A Bandi *Proceedings of the International Symposium on Chemical Fixation of Carbondioxide* Nagoya 2-4 Dec (1991) 439

221 A Bandi, C U Maier, F Philips, J Schefotd, J Schwarz M Speeht and M Vetter *DECHEMA*, Monogr VCH Weinteim (1992) 125

222 A Rodes, E Pastor and T Iwasita, An Quim (1993) 89; 458 *Chem Abstr* 120 (1994) 229696a

223 A Rodes, E Pastor and T Iwasita *J Electroanal Chem* **369** (1990)183

224 (a) B Z Nilkolic, Huang, D Gervasio, A Lin, c Fierro, R R Adzic and E B Yeager, *Ibid* **295** (1990) 415; (b) N Hoshi, T Suzuki, Y Hori *Electrochim Acta* **41** (1996) 1647; (c) N Hoshi, T Suzuki, Y Hori *J Phys Chem B* **101** (1997) 8520; (d) N Hoshi, S Kawatani, M Kudo, Y Hori *J Electroanal Chem* **467** (1999) 67; (e) N Hoshi, Y Hori *Electrochim Acta* **45** (2000) 4263

225 E Morallón, J L Vásquez, A Aldaz and J Calvilier *ibid* **316** (1990) 263

226 A Rodes, E Pastor and T Ivasita *ibid* **373** (1994) 167

227 A Bocarsly, G Seshadri and L Chao *Proc Electrochem Soc* 93-18 (Proceedings of the Symposium on Environmental Aspects of Electrochemistry and Photoelectrochemistry) (1993) pp 30-7; *Chem Abst* **120** (1994) 89191e

228 O Seshadri, Ch Lin and A B Bocarsley *J Electroanal Chem* **372** (1994) 145

229 N Inuzuka *Jpn Kokai Tokkyo Koho* JP 04 311 586 (1992); *Chem Abstr* **120** (1994) 309799b

230 Ch Furuya *Jpn Kokai Tokkyo Koho* JP 07 934 85 (1994); *Chem Abst* **121** (1994) 21038a

231 Ch Furuya *Jpn Kokai Tokkyo Koho* JP 07 258 877 (1994); *Chem Abst* **124** (1996) 17519c

232 B I Podlovchenko, E A Kolyadko and Sh Lu *J Electroanal Chem* **373** (1994) 185

233 B I Podlovchenko, E A Kolyako and Sh Lu *J Electrokhimiya* **30** (1994) 670

234 N Furuya, T Yamazaki and M Shibata *J Electroanal Chem* **459** (1998) 167

235 C Iwakura, S Takezawa, H Inoue *J Electroanal Chem* **459** (1998) 167

236 O Koga and Y Hori *Electrochim Acta* **38** (1993) 1391

237 O Koga and Y Hori *Denki Kagaku* **61** (1993) 812; *Chem Abstr* **119** (1993) 2128055

238 O Koga and Y Hori *Proc Electrochem Soc* 93-18 (Procedings of the Symposium Environmental Aspects of Electrochemistry and Photoelectrochemistry) (1993) pp 11-16

239 A Kudo, Sh Nakagawa, A Tsuneto and T Sakata *J Electro Chem Soc* **140** (1993) 1541

240 H Hara, A Tsuneto, A Kudo and T Sakata, *Shokubai* (1993) 35; *Chem Abstr* **120** (1994) 120194

241 K Ito, Sh Ikeda and M Okabe *Denki Kagaku* **48** (1980) 247

242 K Ito, Sh Ikeda, T Lida and H Niwa, *ibid* **49** (1980) 106

243 Y Hori, O Koga, A Aramata and M Enyo *Bull Chem Soc Jpn* **65** (1992) 3008

244 (a) A Bandi, C U Maier, J Schwarz and M Spectr *DECHEMA* Monogr Chemische Energiegewinnung), **128** (1993) 563; (b) D Walther, M Ruben and S Rau, *Coord Chem Rev* **182** (1999) 67

245 E Moralló, J L Vásquez, J M Pérez and A Aldrz *J Electroanal Chem* **380** (1995) 47

246 S Taguchi and A Aramato *Electrochim Acta* **39** (1994) 2533

247 K Hara, A Kudo and T Sakata *J Electrochem Soc* **142(4)** (1995) L57

248 M W Breiter *Electrochim Acta* **12** (1967) 1213

249 H B Urbach, L G Adams and R E Smith *J Electrochem Soc* **121** (1974) 233

250 J Oiner *Electrochim Acta* **8** (1963) 857

251 J Sobkowski and A Czerwinski *J Electroanal Chem* **55** (1974) 391

252 Idem *ibid* **65** (1975) 327

253 Idem *J Phys Chem* **89** (1985) 365

254 T Iwashita, F C Nart, B Ropez and W Vielstich *Electrochim Acta* **37** (1992) 2361

255 V E Kazarinov, V N Andreev and A V Shelepakov *Electrochim Acta* **34** (1989) 905

256 S Nagakawa, A Kudo, M Azuma and T Sakata *J Electroanal Chem* **308** (1991) 339

257 M Azuma, K Hashimoto, M Hiramoto, M Watanabe and T Sakata *Ibid* **260** (1989) 441

258 M Azuma, K Hashmoto, M Hiramoto, M Watanobe and T Sakata *J Electrochem Soc* **137** (1990) 1772

259 Y Hori, A Murata, R Takahashi and S Suzuki *J Am Chem Soc* **109** (1987) 5022

260 D W Dewulf, T Jin and A J Bard *J Electrochem Soc* **136** (1989) 1686

261 J J Kim, D P Summers and K W Frese Jr *J Electroanal Chem* **245** (1988) 223

262 K Hara, A Kudo and T Sakata *J Electoanal Chem* **386** (1995) 257

263 D P Summers and K W Frese Jr *Ibid* **205** (1986) 219

264 (a) N S Lewis, G A Shreve *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide* (Eds B P Sullivan, K Krist, H E Guard, Elsevier Amsterdam (1993) pp 263–290; (b) H Flaisher, T Tenne and M M Halmann *J Electroanal Chem* **402** (1996) 97; (c) R Hinogami, Y Nakamura, S Yae and Y Nakato *J Phys Chem B* **102** (1998) 974; (d) K Hirota, D A Tryk, T Yamamoto, K Hashimoto, M Okawa and A Fujishima *J Phys Chem B* **102** (1998) 9834

265 M Aulice Scibioh and B Viswanathan, ‘Photo/ Electrochemistry & Photobiology for Environment, Energy & Fuel (Ed S Kaneaco) (Accepted, 2001)

266 M N Mahmood, D Masheder and C J Harty *J Appl Electrochem* **17** (1987) 1223

267 P A Christensen, A Hamnett and A V G Muir *J Electroanal Chem* **241** (1988) 361

268 S Kapusta and N Hackerman *J Electroanal Chem* **131** (1984) 1511

269 H Tanabe and K Ohno *electrochim Acta* **32** (1987) 1121

270 S Meshitsuka, M Ichikawa and K Tamaru *J Chem Soc Chem Commun* (1979) 158

271 C M Lieber and N S Lewis *J Am Chem Soc* **106** (1984) 5033

272 B R Eggins, J T S Irrine and J Grimshaw *J Electroanal Chem* **266** (1989) 125

273 N Furuya and K Malsui *J Electroanal Chem* **271** (1989) 181

274 M Hammouche, D Lexa, M Momenteau and J-M Savéant *J Am Chem Soc* **113** (1991) 455

275 T Yoshida, K Kamoto, M Tsukamoto, T Iida, D schlettwein, D Wöhrle and M Kaneko *J Electroanal Chem* **385** (1995) 209

276 T Abe, T Yoshida, S Tokita, F Taguchi, H Imaya & M Kaneka *J Electroanal Chem* **412** (1996) 125

277 T Abe, F Taguchi, T Yoshida, S Tokita, G Schnurpfeil, D Wöhrle and M Kaneko *J Mol Cat A: Chemical* **112** (1996) 55

278 T Abe, H Imaya, T Yoshida, S Tokita, D Schlettwein, D Wöbrle and M Kaneko *J Porphyrins and Phthalocyanines* **1** (1997) 315

279 P A Vigato, S Tamburrini and D E Fenton *Coord Chem Rev* **106** (1990) 25

280 S Gambarotta, F Arena, C Floriani and P F Zonazzi *J Am Chem Soc* **104** (1982) 5082

281 G Fachinetti, G Fochi, T Funaioli and P F Zanazzi *J Chem Soc Chem Commun* (1987) 89

282 *Electrode materials and processes for energy conversion and storage* (Eds J Zagal, M Paez and C Fierro S Srinivasan, S Wagner and H Wrobloba) **87-12** (1987) 198

283 G H Jeung *Proc Int Conf Coord Chem* **30** (1994) 6

284 N Furuya and S Koide *Electrochim Acta* **36** (1991) 1309

285 T Atoguchi, A Aramata, A Kazusaka and M Enyo *J Chem Soc Chem Commun* (1991) 156

286 T Atoquchi, A Aramata, A Kazusaka and M Enyo *J Electroanal Chem* (1991) 309

287 M Beley, J Collin, R Ruppert and J P Sauvage *J Am Chem Soc* **108** (1986) 7461

288 A R Guadalupe, D A Usifer, K T Potts, H C Hurrel, A Mogstad and H A Abruna *J Am Chem Soc* **110** (1988) 3462

289 J Y Becker, B Vainas, R Eger and L Kaufman *J Chem Soc Chem Commun* (1985) 1471

290 X Cao, G Zheng and Y Teng Caodeng Xuexiapo Huaxue Xuebao **9** (1988) 861 *Chem Absli* **110** (1988) 30397

291 X Cao, Y Mu, M Wang and L Luan Huaxe Xuebao **44** (1986) 220

292 I Bhugun, D Lexa and J M Savéant *J Am Chem Soc* **118** (1996) 1769

293 I Bhugun, D Lexa and J M Savéant *J Phy Chem* **100** (1996) 19981

294 J Zhang, W J Pietio and A B P Lever *J Electroanal Chem* **403** (1996) 93

295 M Bakir and J A M Mckenzie *J Electroanal Chem* **425** (1997) 61

296 S Daniele, P Ugo, G Bontempelli and M Florani *J Electroanal Chem* **219** (1987) 259

297 F R Keene, C Creutz and N Sutin *Coord Chem Rev* **64** (1985) 247

298 J Hawecker, J M Lehn and R Ziessel *J Chem Soc Chem Commun* **536** (1983)

299 J Hawecker, J M Lehn and R Ziessel *J Chem Soc Chem Commun* **328** (1984)

300 J Hawecker, J M Lehn and R Ziessel *Helv Chim Acta* **69** (1986) 1990

301 B P Sullivan and T J Meyer *J Chem Soc Chem Commun* (1984) 1244

302 B P Sullivan, C M Bolinger, D Conrad, W J Vining and T J Meyer *J Chem Soc Chem Commun* (1985) 1414

303 B P Sullivan and T J Meyer *Organometallics* **5** (1986) 1500

304 M R M Bruce, E Megehee, B P Sullivan, H Thorp, T R O’ Toole, A Downart and T J Meyer *Organometallics* **7** (1988) 238

305 H Ishida, K Tanaka and T Tanaka *Chem Lett* (1985) 405

306 H Ishida, H Tanaka, K Tanaka and T Tanaka *J Chem Soc Chem Commun* (1987) 131

307 H Ishida, H Tanaka and T Tanaka *Organometallics* **6** (1987) 181

308 (a) C M Bolinger, B P Sullivan, D Conrad, J A Gilbert, N Story and T J Meyer *J Chem Soc Chem Commun* (1985) 796; (b) C M Bolinger, N Story, B P Sullivan and T J Meyer *Inorg Chem* **27** (1988) 4582

309 H Nagao, T Mizuleawa and K Tanaka *Inorg Chem* **33** (1994) 3415

310 K Tanaka *Proc Int Conf Coord Chem* **30** (1994) 104

311 H Nagao, T Mizuleawa and K Tanaka *Chem Lett* (1993) 955

312 J P Collin and J P Sauvage *Coord Chem Rev* **93** (1989) 245

313 T Yoshida, K Tsutsumida, S Teratani, K Yasufuku and M Kaneko *J Chem Soc Chem Commun* (1993) 631

314 (a) T R O' Toole, B P Sullivan, M R-M Bruce, L D Maugerum, R W Murray and T J Meyer *J Electroanal Chem* **259** (1989) 217; (b) S Cosnier, A Derozier and J C Mocitet *J Electroanal Chem* **207** (1986) 315

315 A I Breikss, H D Abrei_a *J Electroanal Chem* **201** (1989) 347

316 P A Chrislensen, A Hamnett, S J Higgins and J A Timney *J Electroanal Chem* **395** (1995) 195

317 G N A Nallas, K J Brawer *Inorg Chim Acta* **253** (1996) 7

318 (a) C Arana, M Keshavarz-K, K T Potts, H D Abru_a *Inorg Chim Acta* **225** (1994) 285; (b) C Arana, S Yan, M Keshavarz-K, K T Potts and H D Abru_a *Inorg Chem* **31** (1992) 3680

319 K M Lam, K Y Wong, S-M Yang and C M Che *J Chem Soc Dalton Trans* (1995) 1103

320 J A Ramos Sende, C R Arana, L Hernández, K T Potts, M Keshevarz-K and H D Abruna *Inorg Chem* **34** (1995) 3339

321 A G M M Hossain, T Nagaoka, K Ogura *Electrochim Acta* **41(17)** (1996) 2773

322 K-Y Wong, W-H Chung, C-P Lau *J Electroanal Chem* **453** (1998) 161

323 M M Ali, H Sato, T Mizukawa, K Tsuge, M Haga, K Tanaka *Chem Comm* (1998) 249

324 M Aresta, C T Nobile, V G Albano, E Forni and M Manassero *J Chem Soc Chem Commun* (1975) 636

325 M Aresta and C F Nobile *J Electroanal Chem Dalton Trans* (1977) 708

326 T Herskovitz and L J Guggenberer *J Electroanal Chem* **98** (1976) 1615 & 7405

327 R Alvarez, E Carmona, E Gutierrez-Puebla, J M Marin, A Monge and M L Poveda *J Chem Soc Chem Commun* (1984) 1326

328 R Alvarez, E Carmona, J M Marin, M L Poveda, E Gutierrez-Puebla and A Monge *J Am Chem Soc* **108** (1986) 2286

329 J C Calabrese, T Herstovitz and J B Kinney *J Electroanal Chem* **105** (1983) 5914

330 G S Bristow, P Hitcock and M F Lappert *J Chem Soc Chem Commun* (1981) 1145

331a S Slater and J H Wagenknecht *J Am Chem Soc* **106** (1984) 5367

331b A Szymaszek and F P Pruchnik *J Organomet Chem* **376** (1989) 133

332 D L Dubois and A Miedaner *J Am Chem Soc* **109** (1987) 113

333 P A Christensen and S J Higgins *J Electroanal Chem* **387** (1995) 127

334 Y Matsumoto, Y Uchida, M Hidai, M Tesuka, T Yajima and A Tsuchiya *J Electroanal Chem* **104** (1982) 6834

335 (a) M Nakazawa, Y Mizobe, Y Matsumoto, Y Uchida, M Tesuka and M Hidai *Bull Chem Soc Jpn* **59** (1986) 809; (b) T Tomohiro, K Uoto and H Okuno *J Chem Soc Chem Commun* (1990) 194

336 K Ogura and K Tokamagari *J Electroanal Chem Dalton Trans* (1986) 1519

337 K Ogura and I Yoshida *J Mol Catal* **34** (1986) 67

338 K Ogura and M Fujita *J Mol Catal* **41** (1987) 303

339 (a) T Tomohiro, K Uoto and H Okuno *J Chem Soc Chem Commun* (1990) 194; (b)K S Ratliff, R E Lentz and C P Kubiak *Organometallics* **11** (1992) 1986

340 K Ogura, N Endo, M Nakayama and H Ootsuka *J Electrochem Soc* **142(12)** (1995) 4026

341 K Ogura, M Nakayama and C Kusumoto *J Electrochem Soc* **143(11)** (1996) 3606

342 K Ogura, N Endo and M Nakayama *J Electrochem Soc* **145(11)** (1998) 3801

343 S Ogawa, T Vamaguchi and N Gotoh *J Chem Soc Chem Commun* (1972) 577

344 S Ogawa, T Vamaguchi and N Gotoh *J Chem Soc Perkin Trans* (1974) 976

345 S Ogawa *J Chem Soc Perkin Trans* **214** (1977)

346 M Seno, S Tsuchiya and S Ogawa *J Am Chem Soc* **99** (1977) 3014

347 J Lewis and T O'Donoghue *J Chem Soc Dalton Trans* (1980) 736

348 J Costamagna, J Canales, J Vargas, M Camalli and E Rivarola *Pure Appl Chem* **65** (1993) 121

349 J Costamagna, J Canales, J Vargas, A Alvarado and G Ferraudi *J Indn Chem Soc* (1993) 987

350 Perspectives in Coordination Chemistry (Eds R D Hancock A F Williams, C Floriani and A E Merback) VHCH Basel (1992) 129

351 J Costamagna, J Canales, J Vargas and G Ferraudi *Pure Appl Chem* **67** (1995)

352 G Estiu, A Judert, J Molina, J Costamagna J Canales and J Vargas *Inorg Chem* **34** (1980)

353 *The porphyrins* (Ed D Dolphine) Academic Press NY (1978)

354 *Coordination Chemistry of Macrocyclic Compounds* (Ed G A Melson), Plenum NY (1979)

355 M Beley, J P Collin, R Ruppert and J P Sawage *J Chem Soc Chem Commun* (1984) 1315

356 M Fujihira, Y Hirata and K Suga *J Electroanal Chem* **292** (1990) 199

357 J L Grant, K GASWAMI, L O Spreer, J W Otvos and M Calvin *J Chem Soc Dalton Trans* (1987) 2105

358 J P Collin, A Jouaiti and J P Sauvage *Inorg Chem* **27** (1988) 1986

359 G B Balazs and F C Anson *J Electroanal Chem* **322** (1992) 325

360 G B Balazs and F C Anson *J Electroanal Chem* **361** (1993) 149

361 S Sasaki *J Am Chem Soc* **112** (1990) 7813

362 C I Smith, J A Crayston and R W Hay *J Chem Soc Dalton Trans* (1993) 3267

363 H D Abruna, S Yan, K T Potts, M Keshavarz, J A Ramos, L Hernandez, E Cuadrada, M Moran and J Losada *Proc Int Conf Coord Chem* **30** (1994) 122

364 (a) M H Schmidt, G M Miskelly, N S Lewis *J Am Chem Soc* **114** (1992) 2055; (b) A H A Tinnemans, T P M Koster, D H M W Thewissen and A M Macker *Recl Trav Chim Pays Bas* **103** (1984) 288

365 E Fujita, C Creutz, N Sutin and d J Szatda *J Am Chem Soc* **113(1)** (1991) 343

366 M Shionoya, E Kimura and Y Litaka *J Am Chem Soc* **112** (1990) 9237

367 E Fujita, J Haff, R Sanzenbacher and H elias *Inorg Chem* **33** (1994) 4627

368 F Abba, G Desantis, L Fabbrizzi, M Licchelli, A M M Lanfredi, P Pallavicini, A Poggi and F Ugozzoli *Inorg Chem* **33** (1994) 1366

369 G Fachinetti, C Floriani, P F Zanazzi *J Am Chem Soc* **100** (1978) 7405

370 R W Hay, J-A Crayston, T J Cromie, P Lightfoot and D C L deAlwis *Polyhedron* (1997) 3557

371 K Bujno, R Bilewicz, L Seigbried and T Kaden *J Electroanal Chem* **407** (1996) 131

372 C A Kelly, Q C Mulazaani, M Venturi, E L Blinn and M A J Rodgers *J Am Chem Soc* **117** (1995) 4911

373 K Bujno, R Bilewiz, Lsiegfried and T Kaden *electrochim Acta* **142(8)** (1997) 1201

374 E Mejeritskaia, F Luo, C A Kelly, B Koch, E M Gundlach and E L Blian *Inorg Chem Acta* **246** (1996) 295

375 (a) P V Ragini and V R Vijayaraghavan *Bull Electrochem* **12** (1996) 405; (b) P V Ragini *Studies on The Reduction of CO_2 Using Nickel(II)hexaazamacrocycle complexes as Electrocatalysts* Ph D *Thesis* University of Madras, India, June (1994)

376 M Aulice Scibioh and V R Vijayaraghavan *Bull Electrochem* **13** (1997) 275

377 M Aulice Scibioh and V R Vijayaraghavan *Bull Electrochem* **16(8)** (2000) 376

378 (a) M Aulice Scibioh, V R Vijayaraghavan and B Viswanathan *Bull Electrochem* (2001) (in press); (b) M Aulice Scibioh, S Rani and V R Vijayaraghavan *Trans SAEST* **36** (2001); (c) M Aulice Scibioh, P V Ragini, S Rani, V R Vijayaraghavan and B Viswanathan *Indn Acad Sci* (2001) (in press)

379 M Aulice Scibioh *Studies on Electrochemical Reduction of CO_2 Using Nickel(II) Azamacrocycle Complexes as Electrocatalysts at HMDE* Ph D Thesis University of Madras India June (1998)

380 C Alwis, J A Crayston, T Cromie, T Eisenblätter, R W Hay, Y D Lampeka and L V Tsymbal *Electrochim Acta* **45** (2000) 2061

381 *Perspectives Coordination Chemistry* (Eds C Sed and F Vögtler in A F Williams, C Floriani and A E Merbach) VHCH Basel (1992) p 31

382 *Perspectives in Coordiantion Chemistry* (Eds G Denti, S Serroni, S Campagna, A Juris, M Ciano and V Balzani in A F Williams, C Floriani and A E Merbach) VHCH Basel (1992) p 153

383 *Perspectives Coordiantion Chemistry* (Eds G Denti, S Serroni, S Campagna, A Juris, M Ciano and V Balzani in A F Williams, C Floriani and A E Merbach) VHCH Basel (1992) p 203

384 *Perspectives Coordiantion Chemistry* (Eds M W Hosseini in A F Williams) VHCH Basel (1992) p 333

385 *Perspectives Coordiantion Chemistry* (Eds J-M Lehn in A F Williams) VHCH Basel (1992) p 447

386 R Kramer, J-M Lehn, A Decian and J Fisher *Angew Chem Int Ed Engl* **32** (1993) 703

387 A DeBlas, G DeSantis, L Fabrizzi, M Licchelli, A M M Manfredi, P Pallavicini, A-Poggi and F Ugozzoli *Inorg Chem* **32** (1993) 106

388 G DeSanti, L Fabrizzi, M Licchelli, C Mangano and P Pallavicini *Inorg Chem* **32** (1993) 3385

389 E Kimura, M Haruta, T Koike, M Shinoya, K Takenakhi and Y Iitaka *Inorg Chem* **32** (1993) 2779

390 G C Rawle, C J Harding, P Moore and N W Alcock *J Chem Soc Chem Commun* (1992) 1701

391 P G Russell, N Kovac, S Srinivasan and M Steinberg *Electrochem Soc* **124** (1977) 1329

392 Y Hori and S Suzuki *Bull Chem Soc Jpn* **55** (1982) 660

393 Y Hori, K Kikuhi and S Suzuki *Chem Lett* (1985) 1695

394 R L Cook, R C MacDuff and A F Sammells *J Electrochem Soc* **137** (1990) 607

395 D P Summers, S Leach and K W Frene Jr *J Eledronal Chem* **205** (1986) 219

396 K W Frese Jr *J Electrochem Soc* **138** (1991) 3338

397 D R Palmer and R Van Eldik *Chem Rev* **83** (1983) 651

398 (a) N Furuya, K Matsui and S Motto *Denki Kagaku* **55** (1987) 787; (b) N Furuya, K Matsui and S Motto *Denki Kagaku* **56** (1988) 980

399 (a) M Schwarz, R L Cook, V M Kehoe, R C MacDutt, J Patel and A F Sammells, *J Electrochem Soc* **142(4)**, L57p, 1995; (b) Yu B Vassilier, V S Bagotskii, N V Osetrova, O A Khazova and N A Mayorora *J Electroanal Chem* **189** (1985) 271

400 F Fischer and O Prziza *Ber Dtsch Chem Ges* **47** (1914) 256

401 (a) K Ito,S Ikeda and M Okabe *Denki Kagaku* **47** (1980) 256; (b) K Ito, S Ikeda, T Iida and H Niwa *Denki Kayaku* **49** (1981) 106

402 C Iwakura, S Takezawa and H Inoue *J Electroanal Chem* **459** (1998) 167

403 (a) D C - Amoros, J A - Monge and A L - solano *Langmuir* **12** (1996) 2820; (b) D C - Amoros, J A - Monge, M A delaCasa - Lillo and A L - Solano *Langmuir* **14** (1998) 4589

404 J Imari and K Kanako *Carbon* **27** (1989) 954

405 G X Li, K Kaneko, S Ozeki, F Okino and H Jouhara, J Collopd *Interface Sci* **172** (1995) 539

406 J Imai, M Souma, S Ozeki, T Suzuki, and K Kaneko *J Phys Chem,* **95** (1991) 9955

407 K Kaneko, R Cracknell and D Nicholson *Langmuir* **10** (1994) 4606

408 T Yamamoto, D A Tryk, K Hashimoto, A Fujishima and M Okawa, *J Electrochem Soc* **147(9)** (2000) 3393

409 L D Bruke and L M Hurley *Electrochim Acta* **44** (1999) 3451

410 L D Bruke, J A Collins and M A Murphy *J Solid State Electrochem* **4** (1999) 34

411 L D Bruke J A Collins and M A Horgan, L M Hurley and A P O' Mullane *Electrochim Acta* **45** (2000) 4127

412 (a) F H Moser and A L Thomas *The Phthalocyanines* CRC Press Boca Raton Florida **1,2** (1983); (b) R J Blagrove *Auster J Chem* **26** (1973) 1545; (c) A B P Lever *Adv Inorg Chem Radiochem* **7** (1965) 27 B D Berezin in *Coordination Compounds of Porphyrins and Phthalocyanines* Wiley New York (1981); (d) F H Moser and A L Thomas *The Phthalocyanine Compounds* Reinhold Publ Corp New Yark (1963)

413 P A Stuzhin and O G Khelevina *Coord Chem Rev* **147** (1996) 41

414 C C Leznoff and A B P Lever Editors *Phthalocyanines Properties and Applications* **3** VCH New York (1993)

415 (a) T R O' Toole, L D Margerum, D Westmoreland, W J Vining, R W Murray and T J Meyer *J Chem Soc Chem Commun* (1985) 1416; (b) C R Cabrera and H D Abruna *J Electroanal Chem* **209** (1986) 101

416 (a) E K Barefield, F V Lovecchio, N E Tokel, E Ochiai and D H Busch *Inorg Chem* **11(2)** (1972) 283; (b) A M Tait, F V Lovecchio and D H Busch *Inorg Chem* **16(9)** (1977) 2206; (c) F V Lovecchio, E S Gore and D H Busch *J Am Chem Soc* **96(10)** (1974) 3109

417 K R Adam, M Antolovich, L G Brigden, A J Leong, L F Lindoy, P J Baillie, D K Uppal, M McPartlin, B Shan, D Proserpio, L Fabbrizzi and P A Tasker *J Chem Soc Dalton Trans* (1991) 2493