ELECTROCHEMICAL CARBON DIOXIDE REDUCTION - FUNDAMENTAL AND APPLIED TOPICS (REVIEW)

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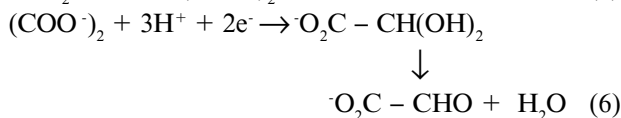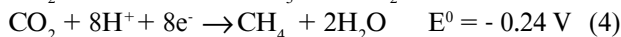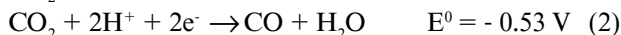*E-mail: mjitaru@chem.ubbcluj.ro*

ABSTRACT

This paper presents the trends on the most important methods for electrochemical reduction of carbon dioxide during the last ten years on metallic cathodes and in the presence of redox mediator systems in aqueous and non-aqueous medium. Other aspects regarding thermodynamics, involved mechanisms   and possible technological use of CO_2 electroreduction were summarized. Of special interest in this review is the discussion of procedures for the selective preparation of formic acid and for the manufacturing of hydrocarbons and/or alcohols using carbon dioxide as a carbon source. The discussion has included both synthetic aspects and mechanistic considerations. The electrochemistry of CO_2 is a continuously growing field. Studies of the poisoning of the electrode surface and investigation of adsorption step are of interest now.

Keywords: carbon dioxide, electroreduction, hydrocarbons, formic acid, mediated electroreduction.

INTRODUCTION

The amount of carbon dioxide in the air has been increasing during the recent years, which may adversely affect the environment in the future. CO_2 is the largest contributor to the greenhouse effect. Moreover carbon dioxide is a very stable,   linear molecule in which the oxygen atoms are weak Lewis bases and the carbon is electrophilic. Reactions of carbon dioxide are dominated by nucleophilic attacks at the carbon, which result in bending of the O-C-O bond.

The most common reactions are as follows*:

$$CO_2 + H^+ + 2e^- \rightarrow HCOO^- \qquad E^0 = -0.61 V \quad (1)$$
$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^0 = -0.53 V \quad (2)$$
$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E^0 = -0.38 V \quad (3)$$
$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^0 = -0.24 V \quad (4)$$

$$2CO_2 + 2e^- \rightarrow (COO^-)_2 \qquad\qquad\qquad (5)$$
$$(COO^-)_2 + 3H^+ + 2e^- \rightarrow {}^-O_2C - CH(OH)_2$$
$$\downarrow$$
$$ {}^-O_2C - CHO + H_2O \quad (6)$$

* (at pH 7 in aqueous solution versus NHE, 25^0C, 1 atmosphere for the gases, and 1 M for the other solutes).

The main reduction compounds are formic acid, methanol, hydrocarbons and oxalic acid. This electroreduction of carbon dioxide is of interest as a potential component of a carbon energy cycle (i.e. CO_2 + energy $\rightarrow$ methane $\rightarrow CO_2$ + energy). The synthesis of hydrocarbons from CO_2 is a complex multi-step reaction with adsorbed intermediates, most nota-

bly adsorbed CO. The possible pathways to obtain chemicals from carbon dioxide are illustrated in Fig. 1.

Photosynthesis, photocatalytic and electrochemical reduction of CO_2 [1, 2] seem to be three of the most effective methods for the processing and recovery of the air carbon based sources. Different energies are needed to break a C-O bond in carbon dioxide, and assist in converting it into useful products. One of them is the electricity in electrochemical reduction processes.

The objective of this paper is to provide a general overview of various pathways for electrochemical carbon dioxide reduction, emphasizing on the last ten years.

THERMODYNAMIC CONSIDERATIONS

The thermodynamic requirements for various CO_2-reduction reactions should be considered (see reactions 1-6) because of the stability and chemical inertness of CO_2. The necessary energy to carry out carbon dioxide transformations for the processing and recovery of the air carbon based sources can be generated by high temperatures, extremely reactive reagents, electricity, or the energy from photons [1].

The potentials for the reduction of CO_2 to CO_2^{-} is -1.9 V vs. NHE, and typical reduction potentials required at either Pt or Hg working electrodes are -2.0 V to -2.5 V, depending on the solvents and electrolytes used. The multielectrons (four-, six-, and eight-electron) charge transfer reductions of CO_2 can be carried out at much more positive potentials than those required for the one-electron reduction.

Hydrogenation of carbon dioxide to methanol is slightly exergonic (ΔG^O = -4.1 Kcal.Mol^{-1}), and to methane to a greater extent (ΔG^O = -31.3 Kcal.Mol^{-1}), because of the favorable thermodynamics of water formation [2, 3].

The barrier to outer-sphere electron transfer for the couple is large because of the very different geometries of the linear, neutral carbon dioxide and the radical anion [4]. The thermodynamic barriers can be reduced by protonating the reduction product. However, because of the close proximity of the hydrogen potential, reduction of H^+/H_2O to H_2 may also occur as a concurrent reaction depending on the system and the electroreduction of carbon dioxide needs substantial overpotentials due to the kinetic barrier and the large difference in the HOMO and LUMO energies.

Moreover, the cathodic reduction of carbon dioxide is normally accompanied by hydrogen evolution and often the mixtures of reaction products are obtained. Accordingly, the main objective of the last papers is to find the electrodes and conditions in order to prepare a majority or a single product.
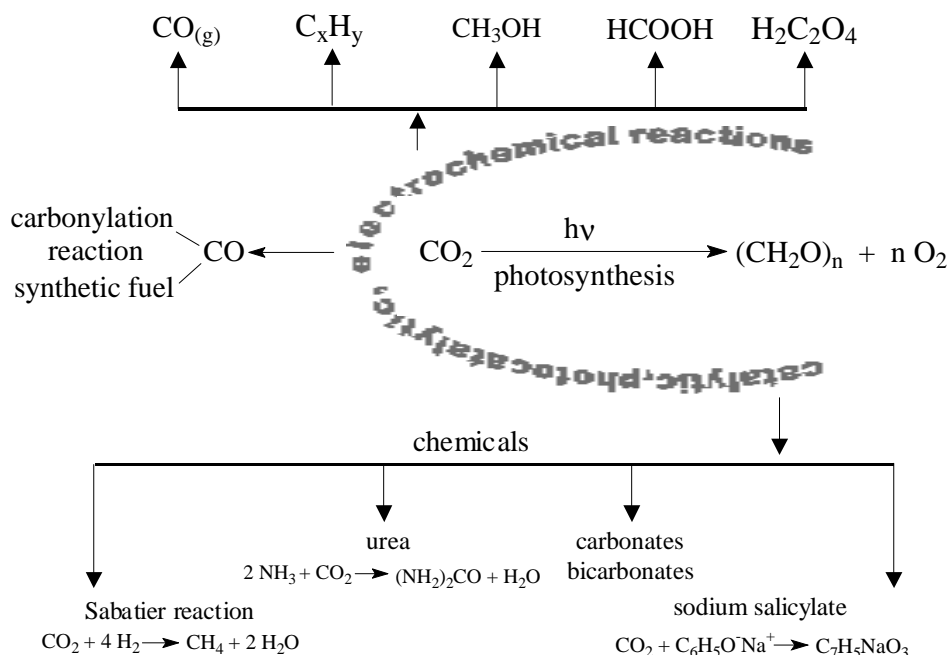
Fig. 1. Possible pathways to obtain chemicals from carbon dioxide.

Table 1. Solubility of CO_2 in various solvents at 25°C.

Solvent	Concentration (M)/conditions
Water	0.033
Methanol	0.06
Tetrahydrofuran (THF)	0.205 ± 0.008
Acetonitrile (AN)	0.279 ± 0.008
Dimethylformamide (DMF)	0.199 ± 0.006
Dimethylsulphoxide (DMSO)	0.138 ± 0.003

The energy requirements are critical for the technological acceptance of the process. If the anodic reaction is water oxidation, the magnitude of the cell voltage is about 3 V, much higher than the energy requirements for water electrolysis.

TRENDS IN ELECTROCHEMICAL CARBON DIOXIDE REDUCTION

The electroreduction of CO_2 is a remarkable process with respect to the primary reasons. Firstly, CO_2 is the ultimate by-product of all processes involving oxidation of carbon compounds and its increasing presence in the atmosphere. Secondly, in the view of the vastness of its supply, CO_2 represents a possible potential source for C-feedstock for the manufacture of chemicals.

The electroreduction of CO_2 at various metal electrodes yields many kinds of organic substances, namely CO, CH_4, C_2H_6, EtOH, other alcohols, etc. Sánchez-Sánchez et al. [1] summarized representative results for the direct electrochemical CO_2 reduction at solid electrodes. The various types of electrocatalytic behaviour among metals can be related to their electronic configuration and can be grouped into *sp* and *d* metals [5]. The electroreduction techniques had to overcome the difficulty of finding electrodes with both a high electrocathalytic activity and a satisfactory lifetime. Also, because of the relatively low solubility of carbon dioxide (Table 1), in aqueous solutions, methods for improving its solubility had to be found. A possible solution of this problem is to perform the electroreduction at a high pressure or in non aqueous solutions.

In our previous publication [5] the most important methods for the electrochemical reduction of carbon dioxide on flat metallic cathodes have been systematically summarized using a novel classification approach. In contrast to the usual classification systems based solely on the products of electrolysis , the electroreduction procedures have been grouped according to both the nature of the cathode (*sp* or *d* group metal electrodes) and the solvent used for the supporting electrolyte (aqueous or non aqueous solutions). The new classification system allows the identity of the electroreduction product to be better related to the nature of the metallic electrode and the supporting electrolyte. Similar reduction products are formed by each of the four possible combinations of electrodes and supporting electrolytes (*sp* group metals in aqueous and non-aqueous electrolyte and *d* group metals in aqueous and nonaqueous electrolytes, respectively). The discussion has included both synthetic aspects and mechanistic considerations. Of special interest in this review is the discussion of procedures for the selective preparation of formic acid and for the manufacturing of hydrocarbons and/or alcohols using carbon dioxide as a carbon source.

In the early seventies, the difference between the electrocatalytic behaviour of electrodes made of *sp* group metals and of *d* group metals, respectively [6-18], was recognized as an important criterion in determining the selectivity of electrode processes. Several classification systems have been used to systematize the impressive number of data accumulated in carbon dioxide related synthetic work [19, 20-23]. Most of these classifications are solely based on the nature of the main product obtained in the electrochemical synthesis. Four classes of metallic electrodes in aqueous supporting electrolytes and three classes for nonaqueous media can be distinguished [20-23]. Thus in aqueous solution: (i) metallic In, Sn,

Hg and Pb are selective for the production of formic acid, (ii) metallic Zn, Au, and Ag produce carbon monoxide, (iii) metallic Cu exhibits a high electrocatalytic activity for the formation of hydrocarbons, aldehydes and alcohols, while (iv) metallic Al, Ga and Group VIII elements (except Pd) show low electrocatalytic activity in carbon dioxide reduction [20-22]. In non aqueous supporting electrolytes (i) on Pb, Tl and Hg the main product is oxalic acid [19]; (ii) on Cu, Ag, Au, In, Zn and Sn carbon monoxide and carbonate ions are obtained [19, 21, 23] 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 [21]. Additional classification criteria for the process occurring in carbon dioxide electroreduction based on both the electrocatalytic properties of the electrode material and the nature of the supporting electrolyte would allow a better systematization of the multitude of reactions and would give more insight into the mechanisms controlling the phenomena.

The main competitive reactions (7-11) involve electrosorbed species with hydrogen atom participation. Thus, in the electrochemical reduction of CO_2 in water, hydrogen formation competes with the CO_2 reduction reaction. Therefore, the suppression of hydrogen formation is very important because the applied energy is wasted on hydrogen evolution instead of being used for the reduction of CO_2.

$$H^+ + e^- \longrightarrow H_{ad} \tag{7}$$

$$CO_2 + H_{ad} \longrightarrow HCOO_{ad} \tag{8}$$

$$HCOO_{ad} + H_{ad} \longrightarrow HCOOH \tag{9}$$

$$HCOO_{ad} + CH_3OH \longrightarrow CH_3COOH + OH_{ad} \tag{10}$$

$$OH_{ad} + H_{ad} \longrightarrow H_2O \tag{11}$$

The large number of recent papers, during the last ten years dealing with the electrochemical reduction of carbon dioxide is of both fundamental and preparative interest.

The main topics of research publications during the last years, illustrated by the number of publications, (Table 2) are:

• electrocatalitic activity for carbon dioxide electroreduction depending on the electrode nature [21, 24-27, 31, 37-39, 40, 44, 45, 53-55, 57, 59];

• influence of aqueous [25, 27, 31, 33, 35, 37, 38, 54, 56, 57, 60] or non aqueous electrolyte [5, 32, 36, 39, 40, 41, 44, 53, 55] on the Faradaic efficiency and/or on distribution of products;

• electrocatalysis by transition metal complexes [24, 52, 55, 58];

• fundamental aspects on the possible mechanism of carbon dioxide electroreduction [24, 53,59,61];

• parameters studies on electrochemical processes for CO_2 reduction [62-66], including deactivation-poisoning aspects during electrolysis [26, 65].

In every category the influence of various specific reaction conditions (potential, buffer strength and local pH, local CO_2 concentration, stirring, and CO_2 pressure, temperature, etc.) on the products formed are presented.

The main topics in carbon electroreduction on flat metallic electrodes seems to be: copper electrodes [26, 34, 39], silver cathode [40], different alloys, Pd-Pt [29] and Ru-Pd [47], conducting polymers [5, 32], other metals, Au [35, 53, 55], Rh [37], polycrystalline Pt [38], Pb[44], modified Ru oxides [46]. Results on the behaviour of some metal diffusion gas electrodes [62-65] based on copper and Cu/Zn oxides [43, 45] for the carbon dioxide electroreduction have been published.

Before arriving to applied processes [65, 66] the technological aspects have been mentioned also in some papers [60, 62-64].

Electroreduction in aqueous medium

A review is provided in 2001 on the aqueous reduction of CO_2 to hydrocarbons at copper electrodes, covering the literature since the first report of the reaction in 1985 [25].

According to this review the reaction product distribution strongly depends on the conditions at which data has been reported. When used in the aqueous solution, most flat metallic electrodes yielded carbon monoxide and formic acid [34, 48]. Only copper was suitable electrode for the formation of hydrocarbons such as methane and ethylene, [31, 33, 54, 57] which can be used as fuel gases. The effect of the low temperature on the Faradaic efficiencies for the products of the electrochemical reduction of CO_2 on Cu in aqueous $NaHCO_3$ solution at -2.0 V is presented in Fig. 2. The selectivity increases enormously with decreasing temperature [48]. Hence, low temperature seems to play a significant role

Table 2. Trends in carbon dioxide electroreduction study (1998-2007).

| Year	Electrode	Experimenat parameters (electrolyte, conditions)	Main Products (Faradaic efficiency, %)	Refs
2007	GC, Cu	$Ru(2,2'\text{-bipyridine})_2(2,2'\text{-bithiazole})^{2+}$	mechanism	24
	granulated Sn, continous reactor	0.5 M $KHCO_3$ + 2 M KCl and 2 M KOH	formate	60
2006	Cu	-	review	25
	-	aqueous	Formate (86)	56
2005	Cu	Deactivation of Cu	CH_4 and other hydrocarbons	26
	Cu+Au	$0.1M$ $KHCO_3$; $0.1M$ K_2SO4	CH_4 (56.9) C_2H_4 (17.1)	54
	Cu polycrystalline	sulfuric and perchloric acid electrolytes	CH_4, C_2H_4 CH_3OH, HCHO	27
	Pt and Pt/C	Competitive adsorption $CO_2\text{-}H_2$	mechanism	59
2004	polypyrrole (PPy) electrode	methanol/ $LiClO_4$	CH_2O(1.9) HCOOH (40.5) acetic acid (62.2)	5
	Pd–Pt–Rh alloys	-	CO	28
	GC	MeCN-water presence of tetra aza annulene]++		52
	Pb-granules	aqueous medium	formic acid (94)	30
	Cu-mesh electrode	Neutral solution	C_2H_4 (80) ; H_2 (9)	31
2003	Au - polycrystalline	DMSO, hexa-aza-macrocycles and its Co(II) complexes	CO and HCOOH	55
2002	-	methanol/$LiClO_4$	-	32
	Cu	aqueous $NaHCO_3$	CH_4 (46)	33
	rhenium and Cu-Rh	(EQCM) with CV	CO, CH_4 (31%)	34
	GC	Methanol- diphthalocyanine complexes and phthalocyanine films	CO, CH_4, $HCOO^-$	58
2001	Au- prepared by sputtering	KCl and $KHCO_3$	CO and H_2	35
	Rhenium electrode-posited on Au	methanol	CO (57), CH_4 (10) and H_2 (33)	36
	Pt porous	perchloric acid	Formic acid, methanol, methane (traces)	37
	Pt - Polycrislaline	Acidic media	-	38
	Au - polycrystalline	DMSO	mechanism	53
	Cu	aqueous	CH_4, C_2H_4	57
1999	Cu	CsOH/ methanol	Methane (8.3), ethylene (32.3), H_2 (23)	39
1998	Ag	KOH-methanol	carbon monoxide and formic	40
	p-InP, p-GaAs photocathode	methanol	CO	41
	Pt, Pd supported GDE	-	methane (38.8)	21
	Pb	KOH/methanol	Formic acid, CO, methane	44
	Cu/Zn oxides	at -1.30 V.	Total reduction (40.5)	45
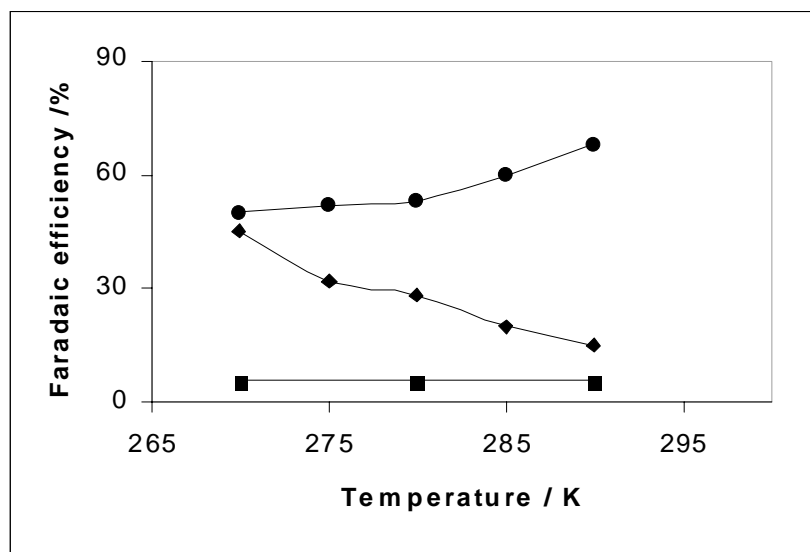
Fig. 2. Faradaic efficiencies for the products formation on Cu electrodes in bicarbonate solution at - 2.0 V, depending on temperature (●) H_2 ; (◆) CH_4 ; (■) HCOOH [34].

in the improvement of the selectivity of CO_2 reduction over H_2 evolution.

The mechanism for the electrochemical reduction of CO_2 in $NaHCO_3$ aqueous solution with a copper electrode was investigated [34]. When the electrolysis was conducted under nitrogen atmosphere, electrolysis yielded exclusively hydrogen. It was established that only dissolved CO_2 molecules take part in the reduction as reducible molecule, and not bicarbonate HCO_3^- or carbonate CO_3^{2-} ions from solution.   Consequently, the targeted products were produced by electrochemical reduction of the CO_2 substrate.

Based on these experimental results and literature reports, the pathways by which methane, ethylene and formic acid on Cu electrode are formed can be estimated, as shown in Fig. 3.

In the reduction system, we assume the usual pathway, one which involves one-electron reduction followed by the disproportionation of $^\bullet CO_2^-$ radical anions to neutral CO molecules and dinegative carbonate ions and by a second electronation/protonation to yield formic acid. In discussing the possible pathways presented in Fig. 3 the localization of the successive electrochemical charge and protons transfers close to the electrode surface has to be considered. The first electrogenerated intermediate is the anion radical ($^\bullet CO_2^-$), which can generate

other active species (CO+OH$^-$ and $^\bullet CH_2$). Thus, the radical $^\bullet CH_2$ has to remain close to the electrode surface in order to be able for the next electron and protons transfers. The large number of mechanisms proposed for the electroreduction of carbon dioxide indicates that this topic has still not been elucidated. Sophisticated mechanistic studies are currently being performed.

On Pt [21, 37, 38, 59] and Rh and Pt-Rh alloys [28] electrodes, at potentials positive to the reversible hydrogen potential, a reaction between CO_2 molecules and atoms of underpotentially deposited hydrogen takes place, the reduction product (mainly CO) becoming adsorbed [29]. CO_2 can be reduced on the surface of Pd-Pt-Rh alloys in the potential range of hydrogen electrosorption. The presence of the adsorbed product of the electroreduction of CO_2 on the electrode surface does not block hydrogen absorption. Hydrogen adsorbed on Pt and Rh atoms is active in CO_2 reduction process, while adsorbed hydrogen bonded to Pd atoms does not participate in this reaction. In contrast to CO_2 behaviour, CO is adsorbed on all alloy components and causes a marked inhibition of hydrogen sorption (both adsorption and absorption)/desorption reactions. Depending on the structure (polycrystalline, porous or supported nano particles) the main reduction products are CO and formic acid.
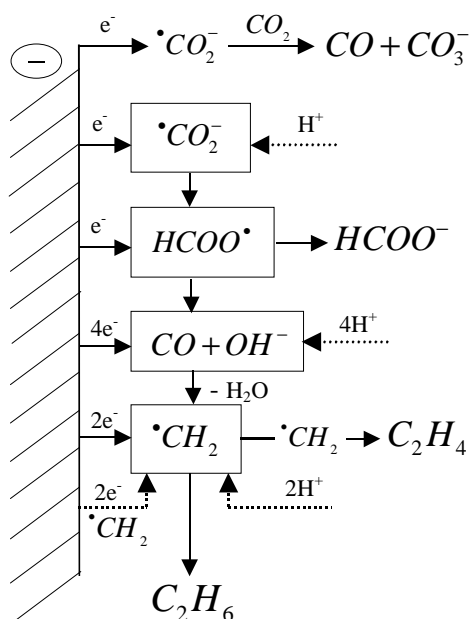
Fig. 3. Pathways for methane, ethylene and formic acid formation on Cu electrode.

Hori et al. [26] with regard to the hydrocarbons formation on copper cathode revealed extended aspects on the deactivation of copper. Many workers reported "poisoning" or "deactivation" of copper electrode in 10-30 min after the start of CO_2 electrolysis.

Features of the deactivation depend greatly on the individual chemical reagents. Purification of the electrolyte solution by preelectrolysis with a Pt black electrode effectively prevents the deactivation of Cu electrode. It is presumed that some impurity heavy metal, originally contained in the electrolyte, is deposited on the Cu electrode during the CO_2 reduction, poisoning the electrocatalytic activity. Not only Cu, but also other electrodes can be poisoned during electrolysis.

The "deactivation" of Cu electrode takes place more or less in all the cases, and the features of the "deactivation" of Cu electrode depend on the reagent used for the electrolyte solution. During long term electrolysis, the "deactivation" is efficiently suppressed if the electrolyte solution is appropriately purified [62, 65]. The same authors mentioned that not only Cu, but also other electrodes can be poisoned during electrolysis. In electrode loses the electrocatalytic activity in CO_2 reduction to formic acid during prolonged electrolyses [68].

Gold electrodes [35, 53-55], have been recently introduced for analytical purposes, namely for the development of a new microelectrode CO_2 sensor. In the described application CO_2 is being electrochemically reduced at unshielded gold microdisc electrodes in DMSO in a standard reaction cell [53].

Spectacular Faradaic efficiencies for HCOOH and oxalic acid have been achieved in high pressure experiments at *sp* group metal electrodes with high overpotential for hydrogen evolution such as Pb [30, 44], p-InP [41] and Cu/Zn oxides [45]. Indium, known for its noteworthy selectivity in the synthesis of formic acid at ambient pressure, has recently been used in high-pressure experiments [75]. Typically, formate ions and hydrocarbon molecules formed on palladium, while the main products on ruthenium were methanol and methane. Copper cathodes are among the most promising options for hydrocarbon manufacturing.

Electroreduction in non- aqueous medium

In organic solvent, there are many studies, because organic aprotic solvents can dissolve much more CO_2 than water, Table 1. Methanol is a better solvent of CO_2 than water, particularly at low temperature, because the solubility of CO_2 in methanol is approximately five times compared to that in water at ambient temperature and eight to fifteen times at temperatures less than 273 K [40].

Several metals that have been previously found inactive in aqueous CO_2 electroreductions have shown, however, some electrocatalytic activity in no aqueous media [12]. It has been found that carbon monoxide, oxalic acid and formic acid were mainly produced from CO_2 in organic solvents such as propylene carbonate and dimethylformamide [69].

Nickel and platinum electrodes in TEAP/PrC electrolyte formed CO and HCOOH (in a ratio from 6:1 to 8:1, wt/wt) at −2.8 V vs. Ag/AgCl. Traces of oxalic acid [21] were also detected. In similar experiments performed on Pd electrodes, significant amounts of oxalic acid (CO/HOOC – COOH = 2:1, wt/wt) and only traces of formic acid were observed [21].

Iron cathodes have proven excellent for the selective preparation of oxalic acid. When used in TEAP/PrC; the HOOC-COOH/CO/H_2 product ratio was approximately 3:1:2 [21]. In DMSO and AN the r_f of oxalic acid was significant (r_f = 50-60 %).

Table 3. Faradaic efficiencies for hydrocarbons preparation on copper: influence of medium and of supporting salts.

Supporting salt, conditions	Main products (Faradaic efficiency, %)	References
KOH/aq	CO (98) hydrocarbons (<2)	39
Benzalkonium chloride	CH_4 (42.5) C_2H_4 (2.4)	50
tetraethylammonium perchlorate/methanol	C_2H_4 (11.5)	51
CsOH (243 K)/methanol	C_2H_4 (23.7-32.3) CH_4 (8.3)	39
$KHCO_3$ (298 K), aq.	CH_4 (16-17.8) C_2H_4 (12.7-14)	49
$KHCO_3$ (273 K), aq.	CH_4 (24.7) C_2H_4 (6.5)	48

Dimerization of $CO_2^{-\cdot}$ anion radical to oxalate ions is prevalent in no aqueous supporting electrolytes (TEAP/PrC).

Due to the extended number of recent papers [32, 36, 39, 25, 44] a special attention has to be paid for electrocatalytic Cu-methanol system [40] and for other cathodes in methanol medium [54, 44, 45, 58].

It was described by Kaneco et al. [34, 39, 40] that Faradaic efficiencies of the products from CO_2 in the methanol were better than those obtained in water. The authors worked at low temperature (248-290K) because the solubility of CO_2 in methanol is strongly depending on temperature and the competitive hydrogen formation diminishes at low temperature.

Judging from the shapes of the voltammograms in electrochemical reduction of CO_2 at Ag electrode in KOH-methanol medium [40] at low temperature the methanol electrolyte provided a large iR potential drop, which may play a significant role in the current-potential relationship. In KOH-methanol, the efficiency of hydrogen formation on Ag electrode was suppressed to less than 3 % at 248 K [40]. The main products are carbon monoxide and formic acid according a usual pathway presented in Fig. 3.

The electrochemical reduction of CO_2 with a Cu electrode in CsOH/methanol-based electrolyte was investigated [39]. The main products from CO_2 were methane, ethylene, ethane, carbon monoxide and formic acid (Table 3). A maximum Faradaic efficiency of the ethylene was 32.3 % at -3.5 V vs. Ag/AgCl saturated KCl. 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 the CsOH/ methanol, the efficiency of hydrogen formation, being a competitive reaction against CO_2 reduction, was depressed to below 23 %. The Faradaic efficiency of ethylene was larger than that of methane in all the potential range. Trace amount of ethane (< 1 %) was formed. The formation efficiency of ethylene was 23.7-32.3 %.

In methanol based electrolyte the low temperature and the electrode nature seem to be important. Thus, in alkaline medium, CO and HCOOH are the main products on Ag electrode [40] and on Cu the predominant formation of ethylene was reported [39].

Mediated electrocatalytic reduction of CO_2

In its most general acceptation, electrocatalysis encompasses the totality of factors modifying the kinetic parameters of the charge-transfer processes in systems involving electrodic interfaces. Thus, mediated

electrocatalysis, ME represents the catalytic effect exerted in the homogeneous phase by a redox system, regenerated by a heterogeneous process at the electrode [14, 22].The mediated electrocatalytic process involves al least two ET steps occurring in the electrochemical cell, at least one of these steps being of heterogeneous nature and taking place at the electrode. The proceeding of ME processes assumes an interaction between mediator - electrode - substrate molecule, carbon dioxide in this paper. The main results of this interaction are: energy gain, important at least from the energetic point of view, decrease of electrochemical potential at which the electrochemical reduction occurs and increase of the selectivity of process.

On the other hand, it is well known that metal cathodes suffer corrosion or passivation problems that avoid its use as electrocatalysts, during long terms electrolysis. For that reasons and looking for cheaper and versatile systems, a number a metal transition complexes have been investigated as catalysts for the reduction of carbon dioxide [52].

Electrocatalytic carbon dioxide reduction was studied in aqueous media on glassy carbon electrode coated with polymeric Co-tetra-3-aminophenylporphyrin [70]. The redox couple responsible for the catalysis is Co (II)/Co (I). In general, the investigated complexes exhibited both metal-based as well as ligand-based irreversible redox processes under carbon dioxide atmosphere. The [Ni(II)-5,7,12,14-tetramethyldinaphtho[b,i][1,4,8,11] tetraaza [14] annulene][++] cation complex showed electrocatalytic effect (observed catalytic currents) in cyclic voltammetric experiments for carbon dioxide reduction over GC electrode. The electrolysis at controlled potential −1.25 V gives carbon monoxide, formic acid and hydrogen. Hydrogen and carbon monoxide are the main products. Depending on the time of electrolysis, the proportion of CO_2 and H_2 varies slightly around 50 %. Formic acid is a minor product [70].

Köleli et al. focused the interest to investigate a polyaniline film at negative potentials in the MeOH/$LiClO_4$ in order to achieve kinetic data and to find out the optimum electrolysis potential of the electroreduction of CO_2 in MeOH/$LiClO_4$ [32].

Possible technological use of CO_2 electroreduction

To render the electroreduction process efficient, high throughput gas diffusion electrodes are needed. The capital costs for such reactors are significantly greater than those needed for the heterogeneous catalytic reduction of CO_2 in packed bed catalytic reactor. However, the much greater specific reaction rates and the versatility of the electrochemical system for obtaining various products argue for the usefulness of electrochemical reduction as means for carbon dioxide reduction/ elimination [62-66]. Several recent papers related to the electrochemistry of CO_2 are of technological interest [71-74]. Copper tube electrodes have been employed for the production of methanol and formic acid [71], and the mechanism of the electrochemical mass reduction of CO_2 to alkanes and ethanol was studied by means of Cu-loaded gas diffusion electrodes [72]. Additional electrodes are explored in high-pressure experiments for obtaining formic acid with elevated Faradaic yields ($\approx 100\%$ on In, 92 % on Sn and 91.2 % on Pb electrodes). The use of an aluminum foil is proposed for the chemical reduction of fluid and/or gas-like components.

CONCLUSIONS

This paper reviewed some selected approaches on electrochemical reduction of CO_2 to convert this polluting gas to various types of fuels (hydrocarbons, methanol) and to potentially carbon source for raw materials (CO). Starting from thermodynamic considerations on the stability of carbon dioxide molecule and from the synoptic presentation of new trends in carbon dioxide electroreduction, we discussed more about the special behaviour of copper electrodes in aqueous and non-aqueous medium. The discussion has included both synthetic aspects and mechanistic considerations.

It has been shown that the products of the electrochemical CO_2 reduction depend on the electrocatalytic activity of the cathodic metal. Of great importance are the composition of the supporting electrolyte (aqueous or no aqueous solutions), and the experimental parameters (cathode potential, current density, temperature and pressure), as well.

The increasing number of patents in this field supports the conclusion that the electroreduction of

carbon dioxide at the industrial scale is no longer an unrealistic dream, but has promising chances of being achieved in the near future, provided that relatively inexpensive electricity is available.

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