

Electrochemical approaches to alleviation of the problem of carbon dioxide accumulation*

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Abstract: The electrochemical reduction of CO₂, which includes a number of different specific approaches, may show promise as a means to help slow down the accumulation of this greenhouse gas in the atmosphere. Two types of approaches are examined briefly here. First, CO₂ can be used as a reagent in the electrocarboxylation reaction to produce organic carboxylic acids, for example, the pharmaceutical ibuprofen. Second, CO₂ can be converted to a fuel, either directly or via synthesis gas. The latter can be produced with reasonably good energy efficiency in a gas-diffusion, electrode-based cell even at present with existing electrocatalysts. Oxygen gas is produced as a by-product. Further work is needed to improve the selectivity and efficiency in this and other approaches.

INTRODUCTION

Although several different types of gases contribute to the greenhouse effect (caused by the accumulation of these gases in the upper atmosphere), CO₂ is the largest single contributor to the effect. If one agrees that this is indeed a problem, and of course, not everyone does, one recognizes that the scale of the problem is vast. Nevertheless, nearly 100 countries all over the world signed the Kyoto Protocol in 1997, pledging to try to decrease these gas emissions. There is little doubt that human activity plays a significant role in global warming: Witness the fact that the beginning of the most recent significant rise in Earth's temperature coincides with the beginning of the industrial revolution.

Chemists have been working on various ways to prevent the accumulation of atmospheric CO₂, including removal, sequestration, utilization, and conversion into fuels [1]. In particular, electrochemical researchers have been making sizable efforts to develop ways to transform CO₂ into useful substances such as fuels or chemicals [2–3]. The past decade or two have seen the growth of the subject, with promising results of electrochemical approaches.

One of the most easily recognizable modes of CO₂ emission involves the generation of electric power. Arguably, one of the most effective approaches is to develop alternate ways to generate electric power, but the use of renewable energy sources, such as solar and wind power, may not be sufficient owing to the rising demand for energy. Thus, we will have to effectively combine renewable systems with fossil fuel-burning systems. This will require that we find ways to utilize the generated CO₂.

This report tries to portray some of the principal electrochemical approaches to the CO₂ problem that have been proposed by various research groups. We begin by explaining two generic electrochemical methods of utilizing CO₂. The first involves the coupling of CO₂ to electrochemically reduced

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organic molecules (electrocarboxylation), with the goal being to find new routes to synthesize chemicals that are interesting from a pharmacological point of view. The second is the direct electrochemical reduction of CO_2 , with the goal being to obtain hydrocarbons, alcohols, or other fuels. This second method can in turn be divided into two groups, according to whether metals or transition-metal complexes are used as catalysts.

On one hand, we emphasize various ways to avoid mass transport limitations in aqueous media due to the low solubility of CO_2 (33 mM at 25 °C at 1 atm CO_2). Thus, when the charge transfer becomes sufficiently fast, the transport rate of CO_2 to the electrode surface determines the overall reaction rate. On the other hand, we address the problem of the selectivity of the CO_2 reaction. More often than not, we face a competition between CO_2 reduction and H_2 evolution in aqueous media owing to the proximity of the standard potentials.

ELECTROCARBOXYLATION

The utilization of CO_2 in the carboxylation of various types of organic compounds has been known for many years; moreover, organometallic chemistry [4] uses CO_2 and Grignard reagents to prepare various types of carboxylated compounds at the laboratory scale. Electrochemical carboxylation [5] offers a great number of advantages, because it is simpler and might be applicable to the preparation of compounds bearing substituents (F, CN, CO_2R , CO, and OR) that are not compatible with the preparation of organometallic compounds. Electrocarboxylation [6] involves the possibility of introducing one or more carboxylic groups into suitable organic starting materials.

This process is carried out saturating with CO_2 an aprotic solvent in which the organic substrate is dissolved. Aprotic solvents are used owing to the participation of radical anions, which are more stable in aprotic vs. protic solvents. Another reason that aprotic solvents are used is their high solubility for CO_2 , as shown in Table 1. Because of this, mass transport limitations are minimized.

The reaction mechanism for electrocarboxylation [8] depends upon the difference between the potential for CO_2 reduction and that for the organic substrate (R). For substrates more easily reducible than CO_2 , two possible pathways have been considered. They have a common first step, producing at the cathode the radical anion of the organic molecule (R^\cdot). Subsequently, in one case the radical anion reacts as a nucleophile with CO_2 forming a carboxylated radical anion, followed by further reduction of the latter at the potential of formation. In the other case, the radical anion reduces via homogeneous electron transfer a neutral CO_2 molecule, followed by coupling of the two radicals (R^\cdot) and (CO_2^\cdot). For substrates less easily reducible than CO_2 , the first step is the cathodic reduction of CO_2 to (CO_2^\cdot), which attacks the organic substrate, followed by a series of complicated homogeneous electron-transfer reactions.

Electrochemical reductive carboxylations have been described for a large number of substrate types, including ketones [9–11], acetylenes [12], olefins [13–15], alkyl halides [16–19], and heterocyclic compounds [20–21]. However, the most important scale-up processes are related to the synthesis of nonsteroidal antiinflammatory drugs (NSAIDs). On one hand, the alkyl, benzyl, and allyl halides are easily electrocarboxylated by a scheme in which the CO_2 comes to the organic molecule and the halide is lost as an anion, yielding the corresponding carboxylic acid. This synthetic route offers a

Table 1 Solubility of CO_2 in various solvents at 25°C [7].

Solvent	Concentration (M)
Tetrahydrofuran (THF)	0.205 ± 0.008
Acetonitrile (AN)	0.279 ± 0.008
Dimethylformamide (DMF)	0.199 ± 0.006
Dimethylsulphoxide (DMSO)	0.138 ± 0.003

scheme for the production of aryl-2 propionic acids such as ibuprofen and fenoprofen. The electrochemical synthesis of fenoprofen and ibuprofen is described by Fauvarque and coworkers [19] beginning from the corresponding aryl halides, in an undivided cell with tetramethylurea (TMU) or dimethylformamide (DMF) as solvents, with the use of a sacrificial metallic anode and a homogeneous nickel catalyst. This was carried out at high yield (ca. 80%) under galvanostatic conditions. The use of sacrificial anodes is important in lowering the extent of the esterification process, because the generated metal ions react with the carboxylate anion, producing an insoluble precipitate, thus avoiding the possibility of the latter acting as a nucleophilic attacking agent on the unmodified halide to produce the corresponding ester.

On the other hand, the electrocarboxylation of ketones yields the corresponding α -hydroxy acids. This synthetic route has been studied in detail for many years [9] because it offers a synthetic scheme for the production of NSAIDs such as ibuprofen and naproxen. The electrochemical carboxylation of 2-acetyl-6-methoxynaphthalene to 2-hydroxy-2-(6-methoxy-2-naphthyl)propionic acid (or hydroxy-naproxen) was described by Wagenknecht and coworkers [11], who used an undivided cell with DMF as the solvent, plus a sacrificial metallic anode. They also increased the CO_2 concentration by working under high pressure. High yield (75% as isolated dried product) was obtained at rather high current density (1150 A m^{-2}). The process conditions were evaluated at 0.2-L, 1-L, and 75-L scales. Although the best results were obtained in the 1-L system, this process demonstrates the utility of electrocarboxylation systems and their possible industrial applications. The use of sacrificial anodes is important to lowering the incidence of dimerization to pinacols and optimizing the yield of α -hydroxy acids in this reaction.

The employment of sacrificial anodes leads to considerable improvement in yields and selectivities and a simpler isolation procedure in the majority of electrocarboxylation processes. However, it is unavoidable that, after the separation of the products, the remaining aqueous solutions contain stoichiometric amounts of the salts of the metals having been used as anodes. Almost certainly, there will be increasingly severe regulation of environmental metal pollution, and this will effectively stop the development of this kind of process as a viable approach to CO_2 utilization. If researchers can develop a way to use this reaction scheme while avoiding the formation of undesirable products, it could provide an economically interesting approach to CO_2 utilization. Because these transformations have as a main purpose the production of fine chemicals, characteristics such as the product yield or ease of isolation are much more important than, for instance, the current efficiency.

DIRECT ELECTROCHEMICAL REDUCTION

Direct electrochemical approaches to convert CO_2 to various types of fuels have been investigated for several decades. This approach must take into account the possibility of substantial overpotentials due to the kinetic barrier afforded by the large difference in the HOMO and LUMO energies. Moreover, the reduction of carbon dioxide in the potentials at which the cathodic reaction occurs is normally accompanied by hydrogen evolution. Also, the reaction products are often mixtures. The main objective is to develop an electrode that operates at close to the reversible potential for the production of a single product. This paper reviews some selected approaches.

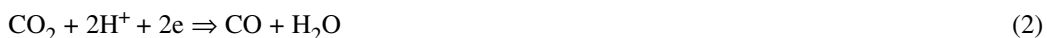
Investigations on the direct electrochemical reduction of CO_2 [22] can be categorized into two groups according to the type of catalytic system:

1. Heterogeneous catalytic systems using cathodes of bulk or particulate metals, which show particular selective product properties. Their general properties are long-term reliability and acceptable mechanical, thermal, and chemical stability.
2. Homogeneous and heterogeneous catalytic systems using transition-metal complexes as catalysts. Attractive features are high selectivity and low operating potentials, but at the price of limited stability.

Heterogeneous catalytic systems using cathodes of bulk or particulate metals

These catalytic systems [23] rely on catalytic metals to carry out the electrochemical reduction of CO₂, and the product selectivity depends on the electrocatalytic activity of the particular metal. The detailed mechanistic pathways for each product are not completely clear at present, and in many cases several different schemes have been proposed. In aqueous solution, C₁-type compounds (e.g., carbon monoxide, formic acid, methanol, methane) are produced. In general, more complex compounds (e.g., oxalic acid, glyoxylic acid, tartaric acid) are produced in nonaqueous solution. Given the influence of the solvent on the nature of the products, it is reasonable to propose two main routes for direct CO₂ electrochemical reduction based on whether the medium is aqueous media or nonaqueous.

The most common reactions are as follows:



Electroreduction in aqueous media

In the case of aqueous media, metal electrodes used in the electroreduction of CO₂ can be divided in different groups according to the nature of the main product [24–25].

- A. Hydrocarbons and alcohols (Cu).
- B. Carbon monoxide (Au, Ag, Zn, Pd, and Ga).
- C. Formic acid (Pb, Hg, In, Sn, Bi, Cd, and Tl).
- D. Some metals do not exhibit useful catalytic properties under typical reaction conditions, e.g., 1 atm CO₂ partial pressure, 25 °C (Ni, Pt, Fe, Co, Rh, Ir, and W). However, this situation can change when the conditions are modified.
- E. Some metals heavily favor hydrogen evolution even if the reaction conditions are modified (Ti, Nb, Ta, Mo, Mn, and Al).

Furthermore, the various types of electrocatalytic behavior among metals can be related to their electronic configuration and can be grouped into sp and d metals. These classifications can be modified through alloying [26]. This modification can be due to a combination of changes in the electronic structure and changes in the surface crystallographic characteristics, including the introduction of dislocations and vacancies. There can be major changes in the product distributions and reaction rates. An interesting example involves metal-hydrogen alloys such as Pd-H. The latter exhibits an enhancement of CO₂ reduction compared to the unalloyed metal. Fujishima and coworkers [27,28] found that the absorption of hydrogen on palladium electrodes enhances the CO₂ electroreduction yield, because the overpotential for H₂ evolution is increased by hydrogen absorption on the Pd electrode.

Examining other factors, several studies have related the current efficiency of CO₂ electroreduction to the nature of the cation and anion present in the supporting electrolyte [29]. Results show that small alkali metal cations (hydrophilic environment) are not adsorbed at the electrode surface, due to their hydration sphere. This improves the current efficiency of CO₂ electroreduction and also shows that nonmetallic cations (hydrophobic environment) enhance hydrogen evolution. However, it should be noted that the same trend is not necessarily true for nonaqueous electrolytes such as methanol.

Because of the low solubility of carbon dioxide in water (33 mM at 25 °C under 1 atm of CO₂), the experiments were conducted under continuous CO₂ sparging, and the current density is typically limited by the diffusion of CO₂ from the bulk to the electrode surface during the electrochemical reac-

tion. Methods designed to avoid this mass transport limitation have been studied. Some selected results are described below.

Low temperature operation

Because the CO₂ solubility in water is significantly higher at low temperatures, it is advantageous to sparge the electrolyte under such conditions [25,30]. It was observed that the reduction efficiency of certain metals increases dramatically. It was also observed that the product ratio at low temperature for other metals was quite different from that at room temperature (Ni, Ag, Cu, Cd, Pb,...). These improved CO₂ reaction yields, might be explained by the combined effect of the increased CO₂ solubility and the increased stability of the reduction intermediates at low temperature.

High-pressure operation

Saturating the electrolyte with CO₂ at high pressure takes advantage of the improved solubility in water [31–35]. The electrode materials can be divided into three groups depending on the kind of effect that the high pressure CO₂ produces on their respective electrocatalytic activities. In the first group of metals, for which hydrogen is the major product at 1 atm pressure (Fe, Co, Ni, Pt, C, W, Rh, and Ir), the high pressure leads to high Faradaic efficiencies for CO and HCOOH. In the second group, (Ag, Au, Zn, In, Pb, Sn, and Bi), the high pressure improves the Faradaic efficiency for CO and/or HCOOH, but the product selectivity is not changed. In the third group, consisting of a single member (Cu), the high pressure changes the CO₂ electroreduction product selectivity from hydrocarbons to CO and HCOOH. In addition, one of the effects of high pressure is to obtain large partial current densities for CO₂ electroreduction. Some representative results are presented in Table 2.

Table 2 Representative results for the direct electrochemical CO₂ reduction at solid electrodes.

Electrode	Ag	In	Cu	Ag	Cu	BDD
Electrolyte	KHCO ₃	KHCO ₃	KHCO ₃	KOH	TBABF ₄	TBABF ₄
Solvent	H ₂ O	H ₂ O	H ₂ O/USI	CH ₃ OH	CH ₃ OH	CH ₃ OH
T (K)	298	298	273	248	298	298
P (atm)	30	60	1	1	40	40
Product	CO	HCOOH	CH ₄	CO	CO	CO
CE (%)	76	108	40	90	87	42
PCD (mA cm ⁻²)	151	215	10	18	288	84
Potential (V)			-1.9	-6.0	-2.3	-4.0
Ref. electrode			SCE	SCE	Ag	W
Author	Hara	Todoroki	Ohta	Kaneco	Saeki	Aoyagi
Year	1995	1995	2000	1998	1995	2000

Abbreviations: CE (current efficiency); PCD (partial current density); USI (ultrasonic irradiation); TBABF₄ (tetrabutylammonium tetrafluoroborate); BDD (boron-doped diamond).

Ultrasonic radiation

Ohta and coworkers have studied the effect of ultrasonic irradiation on CO₂ reduction [36]. They demonstrated that the mass transport rate of CO₂ near the electrode increased under ultrasonic irradiation. In addition, the hydrogen formation was depressed by ultrasonic irradiation.

Gas diffusion electrodes

Because the maximum current densities possible for electrochemical CO₂ reduction at solid electrodes are limited by mass transport, the reaction rates and selectivities for this reaction have been investigated at gas diffusion electrodes (GDEs) catalyzed by various metals and alloys. Such electrodes, often based upon polytetrafluoroethylene (PTFE) as a binder, have been developed to overcome similar mass transport limitations in fuel cells and are capable of operating at high current densities at atmospheric

pressure. Their development has demonstrated the advantages of high surface area catalysts and catalyst supports, together with the unique three-phase interface structure (gas, liquid, solid) as shown in Fig. 1. This structure operates efficiently due to the very short distances that the dissolved gas must travel through the liquid phase in order to react at the solid electrode phase.

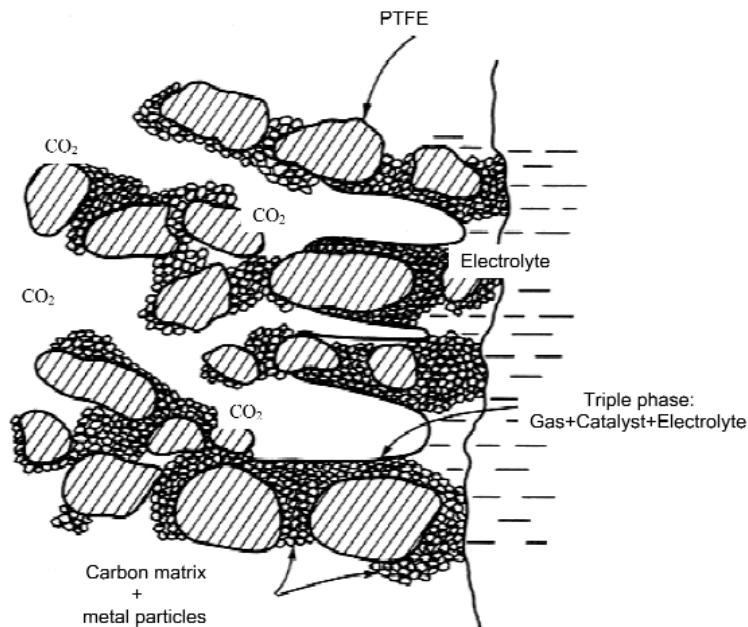


Fig. 1 Schematic diagram of a gas-diffusion electrode active layer.

One disadvantage of GDEs compared to solid electrodes is the possibility of shorter lifetimes. This problem can arise due to slow changes in the complex interfacial structure, due to chemical and physical stresses. Several studies of CO₂ electroreduction have examined various types of GDEs catalyzed by metals and alloys in aqueous media [37–39]. It has been found that, for the most part, the expected efficiency and selectivity is not radically different from that of the bulk electrode material. However, the product partial current densities are often considerably higher than those obtained for the corresponding solid electrodes (see Table 3). Results obtained under high-pressure conditions at solid electrodes are often more comparable with GDE results.

Shibata and coworkers have developed an important line of research involving the electrochemical synthesis of urea by simultaneous reduction of CO₂ and nitrite or nitrate on GDEs with various metal catalysts [40–41]. This is promising as a potential new route with which to employ the products of direct CO₂ electroreduction as an intermediate step in a more complex synthesis scheme to obtain other useful products such as urea.

Hara and coworkers have investigated the possibility of joining GDEs with the favorable high-pressure CO₂ effect in the electrochemical reduction of CO₂ [42–44]. In the same way as that already described for bulk metal electrodes, the results obtained form three different groups, depending on the electrocatalytic activities of the metal catalysts. It was found that certain metals shift from one group to another when CO₂ electroreduction is carried out at a GDE under high pressure. Thus, Ag and Cu do not shift, exhibiting the same product selectivity as that for the solid electrode under high pressure. In contrast, Pt, which belongs to the group of metals in which hydrogen is the major product at 1 atm pressure, both for solid and for GDE, under high pressure supports high Faradaic efficiencies for HCOOH at the solid metal electrode. For a GDE operating at elevated pressures, Pt changes its selectivity to yield

Table 3 Representative results for direct electrochemical CO₂ reduction at gas-diffusion electrodes.

Electrode	Ag	Pb	Pt	Cu	Ru-Pd	Ag	Ni/ACF
Electrolyte	KHCO ₃	Na ₂ SO ₄	KHCO ₃	KOH	KHCO ₃	KOH	KHCO ₃
Solvent	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O
T (K)	298	293	298	275	298	298	298
P (atm)	20	1	30	1	1	30	1
Product	CO	HCOOH	CH ₄	C ₂ H ₄	HCOOH	CO	CO
CE (%)	86	89	35	69	90		67
PCD (mA cm ⁻²)	258	50	313	268	72	3050	60
Potential (V)	-1.22	-1.8	-1.92	-3.0	-1.1		-1.6
Ref. electrode	Ag/AgCl	SCE	Ag/AgCl	Ag/AgCl	NHE		SCE
Author	Hara	Mahmood	Hara	Cook	Furuya	Hara	Yamamoto
Year	1997	1987	1995	1990	1997	1997	2000

Abbreviations: CE (current efficiency); PCD (partial current density); ACF (activated carbon fiber).

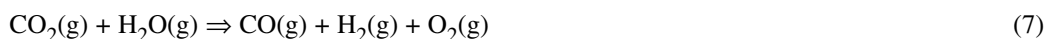
CH₄ as the major product at large partial current densities. Interestingly, this unusual behavior was obtained in a reverse arrangement of the Pt-GDE in the electrochemical cell, i.e., with the hydrophobic side exposed to the electrolyte and the catalytic Pt layer exposed to the gas phase. This may be due to an unexpected effect in which a very thin electrolyte film is in contact with the CO₂ gas.

Novel types of gas diffusion electrodes designs based on inorganic (e.g., Prussian blue) and organic polymer (e.g., polyaniline) films have been tested in the CO₂ electroreduction [45]. These show no usually main products such as ethanol and lactic acid.

Yamamoto and coworkers have investigated the use of activated carbon fibers (ACFs) as a microporous (actually nanoporous, because the slit-shaped pores are on the order of 2 nm wide) catalyst support for GDEs for CO₂ electroreduction [46]. The catalysis involves a so-called “nanospace effect,” which allows high-pressure conditions to be mimicked inside the fibers at ambient pressure. The benefits of the effective high-pressure conditions were evident for ACF/Ni gas diffusion electrodes, i.e., ACF with Ni nanoparticles deposited within the nanopores. The results are reasonable, because the product current efficiency values are comparable with those obtained under high CO₂ pressure conditions at a solid Ni electrode. The principal products were H₂ and CO, suggesting the possibility of producing synthesis gas electrochemically with a controllable CO/H₂ ratio in a single step [47]. This control is available by varying the potential applied to the ACF/Ni-GDE. Thus, various compositions of synthesis gas can be produced. For example, with a 2:1 ratio, it would be useful to synthesize methanol, which in turn could be utilized in fuel cells for electric power generation.



It is useful to consider the possible efficiencies of full electrolytic cells for the production of synthesis gas. This has been done recently experimentally in a flat-type rectangular cell designed to minimize the resistive voltage losses of the electrolyte [47]. The overall reaction produces oxygen at the counter electrode. With a 1:1 CO:H₂ gas composition, the reaction is as follows:



The electrolyte is 0.5 M KHCO₃, which is commonly used in aqueous CO₂ reduction systems, because it maintains the same composition and pH, due to the carbonic acid-bicarbonate equilibrium, during electrolysis. With an ACF/Ni GDE, a cell voltage of 3.05 V was obtained at approximately 10 mA cm⁻², yielding an efficiency of ca. 45%, based on the enthalpic voltage (converting the enthalpy directly to a voltage) of 1.36 V.

It is, of course, necessary to compare such an electrochemical method for producing synthesis gas with purely chemical ones such as steam reforming of methane or partial oxidation of methane, which

is used in industry as a method of producing synthesis gas, and carbon dioxide reforming of methane [48]. Although the electrochemical route costs more energy, this is because it includes the energy cost of producing the hydrogen.

Electroreduction in nonaqueous media

Nonaqueous media present certain advantages for CO₂ reduction: higher CO₂ solubility than that in water, the suppression of hydrogen evolution, and the possibility to work at low temperatures, e.g., below the freezing point of water. In nonaqueous solvents such as DMF, DMSO, or AN, it has been found that several metals that had been found to be inactive in aqueous media have shown significant activity. Although the main products from CO₂ electroreduction in nonaqueous media have been found to be quite similar to those in aqueous media, i.e., carbon monoxide, oxalic acid and formic acid [49–51], the reaction mechanisms can follow pathways different from those in water. For instance, CO can be produced via a reductive disproportionation of CO₂ [52].

Some of the most potentially useful results have been reported in methanol media with various solid metal electrodes. As a first example, Kaneco and coworkers have examined the direct utilization of the industrial methanol-based CO₂ absorber medium as the solvent for the electroreduction process [53–56]. Methanol is a much better solvent for CO₂ than water, particularly at low temperatures. Generally, it has been found that the efficiency of hydrogen evolution decreases with lowered temperature, and therefore the current efficiency for CO₂ reduction increases significantly, just as in aqueous media. Metal-hydrogen alloys such as Ti-H were tested in KOH-methanol media at low temperatures [57]. As with such alloys, e.g., Pd-H, in aqueous media, these exhibited enhancements in the CO₂ electroreduction yield due to the absorption of hydrogen.

CO₂ electroreduction under high pressure (<60 atm) in methanol has been shown to be capable of supporting very large current densities, even at solid metal electrodes [58–61]. One of the more interesting aspects of this research has been the supporting electrolyte effect, specifically the role that the cation plays [59,62]. It has been demonstrated for the solid Cu electrode that the use of a hydrophobic cation such as tetrabutylammonium (TBA⁺) leads to CO as a main product, whereas a hydrophilic cation such as Li⁺ leads to formate and hydrogen as main products [60]. The TBA⁺ cation may form an ion pair with the CO₂ radical anion, stabilizing it. In continuing research in this area, the most promising electrode materials have been found to be silver and diamond, upon which high selectivities and high partial current densities are found for CO production (see Table 2).

Homogeneous and heterogeneous catalytic systems that make use of transition-metal complexes

Transition-metal complex-based catalytic systems have received much attention for CO₂ electroreduction due to the possibility of achieving very high selectivities and activities (see, for example, ref. 63 and references therein). These are usually thought of as operating in a homogeneous phase, dissolved in the reaction medium, in which they act as redox mediators in the CO₂ reduction process. However, such complexes can also operate in a heterogeneous mode, in which the complex is deposited on a solid electrode surface or on a gas diffusion electrode surface. Typical metal complexes involve either square planar or octahedral coordination and make use of metals such as Ni, Re, Pd, Ti, Co, Ru, Rh, Ag, As, Ir, and V and ligands such as porphyrins [64–65], phthalocyanines [66–68], tetrazamacrocycles with or without substituents [69–70], phosphines [71], polypyridines [72], and sulfur clusters [73–74]. In general, the behavior of these complexes is such that square planar complexes tend to catalyze CO₂ reduction in aqueous media, whereas octahedral complexes tend to be more active in nonaqueous media.

Although CO and HCOO⁻ are typical products from the electrochemical reduction of CO₂ catalyzed by metal complexes, other products are also found, depending on the type of catalytic system. The types of products obtained are influenced by the nature of the metal, of the ligand and of the charge distribution in the complex. The binding of CO₂ to the complexes should take place in an axial position

on the reduced central metal ion; depending on the linkage mode, i.e., on a carbon or oxygen of the CO₂ molecule, various products can be expected. The formation of a metal–carbon bond is the intermediate step for the production of CO, while a metal–oxygen bond is the intermediate step for the production of HCOO⁻.

Although some of these complexes have high selectivity and catalytic activity, they lack stability, and, therefore, this is a challenge that must be met to enhance the possibility of their eventual application.

CONCLUSIONS

It appears possible that the electrochemical reduction of CO₂ could be applied to new energy storage systems that could contribute to the alleviation of the accumulation of atmospheric CO₂. As one example, CO₂ reduction shows great potential in the production of pharmaceuticals and fine chemicals. In this type of application, the selectivity is more important than the efficiency. A second example is the reduction of CO₂ to produce fuels or synthesis gas. In this application, both selectivity and efficiency are highly important. The present report has tried to give a flavor for the breadth and range of possibilities in these fields.

As a final word, we would like to encourage anyone interested to join in these efforts, to find new approaches, or to support these lines of research in some manner. We suggest that the key to ultimate success will involve multidisciplinary approaches.

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