

Chapter 2

Electrocatalytic Reduction of CO₂

Renewable sources, such as solar and wind electricity, are attractive alternatives to fossil energy, because they are CO₂ neutral and, therefore, do not contribute to the greenhouse effect. However, these types of renewable energy are not available on demand due to their transient character. Therefore, there is a need in energy storage. Electrical grids can definitely absorb certain supplies of renewable electricity but there is a limit. The grid has to have a certain baseline that assures reliability of power supply. This baseline supply is typically realized through the use of large-scale fossil fuel, nuclear, and hydroelectric power plants, which cannot be easily switched off and on but have to be operated continuously. As more and more renewable sources are being connected to the electrical grid, the problem of electricity oversupply will eventually become the reality.

One option is to store this surplus electricity as a liquid fuel that has high volumetric energy density and can be easily transported, for example methanol. This power-to-fuel chain can be achieved indirectly, using electrolysis and thermocatalytic conversion, or directly by electrochemical reduction. In the first approach, renewable electricity is used to electrolyze water into hydrogen (H₂) and oxygen (O₂) as a valuable by-product. The generated hydrogen is then reacted with CO₂, e.g., via the water gas shift reaction to generate syngas (a mixture of CO and H₂), which can be in turn converted in a variety of value-added products. This pathway was discussed in Chap. 1.

An alternative pathway combines water electrolysis with CO₂ hydrogenation in an electrochemical cell fed with H₂O and CO₂ to produce liquid compounds such as formic acid and methanol. Such conversion technology, if implemented on a large scale, would recycle the otherwise emitted CO₂ into usable fuels, positively affecting the global carbon balance. It is also possible to reduce CO₂ into CO in an electrochemical reactor, therefore producing syngas. However, this approach is less attractive since the thermocatalytic reduction of CO₂ to CO is much more efficient in terms of conversion, throughput, and compactness.

It should be emphasized at this point that dramatic improvements have been recently made in the design of photovoltaic devices leading to improved efficiency and significantly lower production costs. As a result, photovoltaic cells, alongside with wind turbines, are now commercially available and economically viable for small-to-medium scale power generation applications. On the other hand, efficiencies of electrochemical cells for CO₂ reduction to methanol and other liquid chemicals, such as formic acid, remain relatively poor. Improvements could be made through the development of highly efficient catalysts and advanced technological solutions for the electrochemical cell design to achieve high current density operation.

First demonstrations of electrochemical reduction of CO₂ date back to the 19th century and this topic has received a lot of renewed attention since the 80s of the 20th century due to the rapidly rising prices of fossil fuels. Since then, there is a continuous interest in this technology that represents a strategic pathway for conversion of CO₂ into fuels and chemicals including important feedstocks for chemical industry such as formic acid (HCOOH) and methanol (CH₃OH).

Research efforts on the electrochemical reduction of CO₂ have grown rapidly in the last few decades and the potential is enormous. However, the challenges are great. First of all, CO₂ is an extremely stable molecule, very difficult to activate. Activating the CO₂ molecule into its useful state by reduction requires not just a significant energy input but also highly active catalysts. Second, CO₂ solubility in aqueous environments required for electrochemistry is relatively low. These limitations pose fundamental challenges related to chemical catalysis, electrochemistry, and electrochemical cell engineering.

Below, the basic concept of the electrochemical reduction of CO₂ is explained first and the most fundamental challenges are addressed. The discussion focuses then on the CO₂ reduction catalysis and electrochemical cell design. Methanol synthesis is reviewed in more detail, as one of the most promising applications. Syngas production using solid oxide fuel cells is also addressed. In closing remarks, the feasibility of the electrochemical reduction of CO₂ for industrial applications is critically discussed.

2.1 Basics of Electrochemical Reduction of CO₂

In this section, basic principles of the electrochemical reduction of CO₂ in aqueous environments are briefly discussed. For more detailed information, the reader is referred to a number of excellent reviews [1–6]. In the electrochemical reduction of CO₂, electricity is supplied to an electrochemical cell containing an aqueous solution containing dissolved CO₂. The reduction of CO₂ occurs on the cathode and it is balanced by the electrolytic dissociation of water on the anode supplying the protons needed to hydrogenate CO₂ through a proton exchange membrane, as it is schematically depicted in Fig. 2.1, for the case of the CO₂ reduction to CO [7].

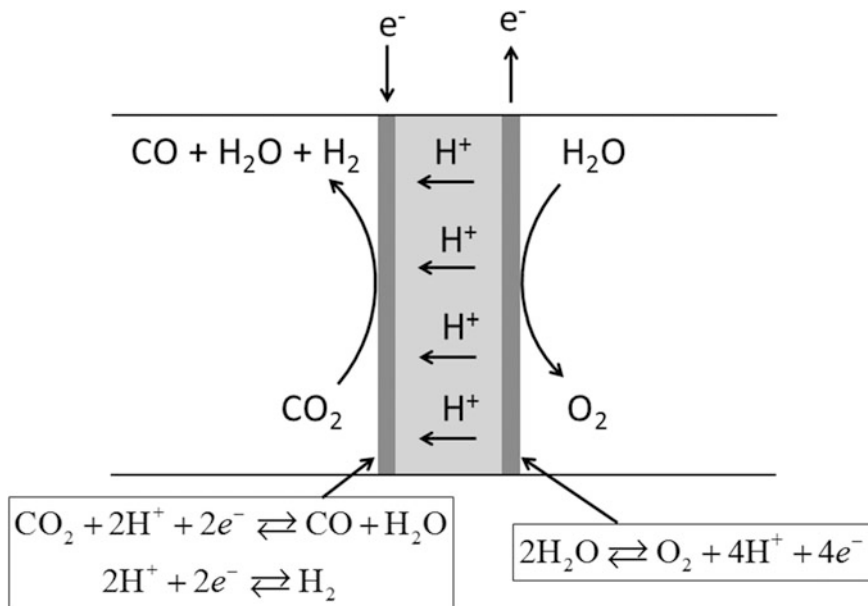
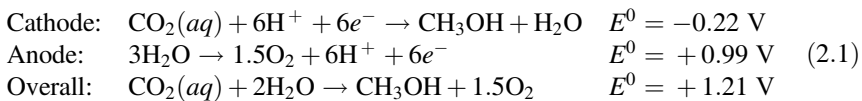


Fig. 2.1 Electrochemical cell with a cation-exchange membrane CEM as electrolyte. The design is similar to a proton-exchange membrane fuel cell

Looking at another example, of CO₂ conversion to methanol (CH₃OH), we find that the reduction and oxidation occurring on the cathode and anode, respectively, are described by the following reactions, showing the overall reaction as well (potentials are shown vs. saturated calomel electrode) [6]:

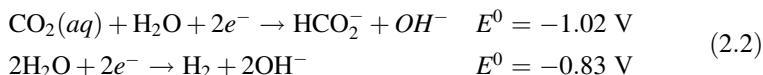


To accelerate the reaction rates, a catalyst is typically deposited on the electrode surface. Catalysis for the electrochemical reduction of CO₂ and the electrochemical cell design are discussed in Sects. 2.3 and 2.4, respectively.

Hereafter, we focus on the cathode side, which is the limiting factor in the electrochemical cell performance. To supply CO₂ continuously to the electrochemical cell, it can be simply bubbled through the solution. However, the limited solubility of CO₂ poses a significant challenge, which will be addressed and discussed in detail in next section. Typically, the electrochemical reduction of CO₂ is carried out in neutral or slightly alkaline solutions because such environment facilitates the formation of the formate ion (HCO₂⁻), which is a reaction intermediate in the CO₂ hydrogenation pathway. In more alkaline solutions, above pH = 9, the formation of the bicarbonate and carbonate ion will be facilitated, limiting the participation of CO₂ in the reduction reaction pathways. Lowering the pH of the

electrolyte allows for dissolving more CO₂/H₂CO₃. However, acidic electrolytes facilitate the H₂ evolution reaction, while hindering the formation of the formate ion. There is still debate between researchers regarding the optimal pH of the electrolyte for the electrochemical reduction of CO₂.

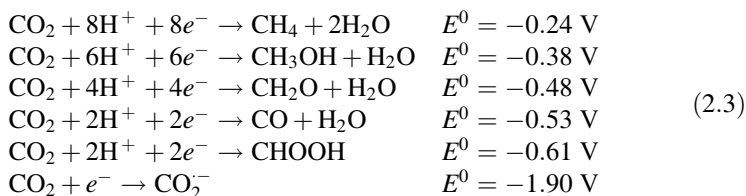
While the electrochemical reduction of CO₂ is feasible thermodynamically, the reduction potential of CO₂ is only slightly different from that for water reduction. As a result, there is a competition between the CO₂ reduction and the more thermodynamically favored H₂ generation (potentials are shown versus standard hydrogen electrode, at 25 °C and pH = 14):



Therefore, the electrical energy supplied to an electrochemical cell will be consumed by two competing reduction mechanisms: H₂ generation via water electrolysis and CO₂ reduction into a product of interest, e.g., methanol or formic acid. High selectivities to the desired product (typically defined as the Faradaic efficiency) and, therefore, high production rates of that desired product can only be achieved if the electrode material suppresses H₂ generation so that most of the supplied electricity is consumed in the CO₂ reduction reaction.

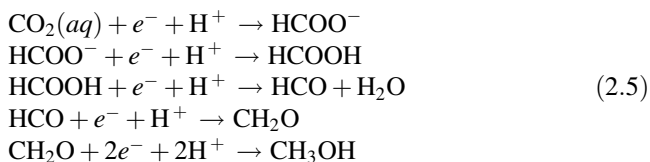
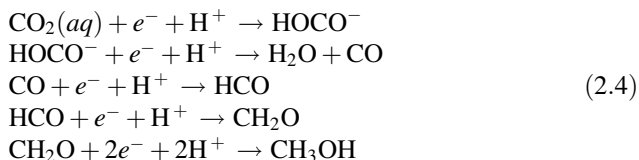
Certain cathode materials, such as Indium (In), Tin (Sn), and Lead (Pb), are known to kinetically suppress H₂ formation. The mechanism of this suppression is the existence of the high water reduction overpotential that results in low exchange current densities. On the other hand, these materials are known to have a relatively good exchange density for the reduction of CO₂. Therefore, even though H₂ formation is more favorable thermodynamically than the electrochemical reduction of CO₂, the formate ion can be produced quite efficiently given a suitable cathode material that limits the water reduction kinetically, while not suppressing the CO₂ reduction to same extent.

In addition to the water reduction, there are a number of other competing reactions occurring during the electrochemical reduction of CO₂. Possible reaction pathways, including the methanol, formic acid and formaldehyde formation, are listed below alongside with corresponding reduction potentials (shown versus normal hydrogen electrode, at 25 °C and pH = 7):



Depending on the product of interest, some of the reactions listed above are called “parasitic reactions”. These undesirable reactions consume the electrical current supplied to the electrochemical cell, reducing the amount of the current consumed

in the desired reaction pathway. Note that the single electron reduction of CO₂ is less favorable than the proton-coupled multi-electron pathways, which is in fact beneficial for the CO₂ reduction into liquid fuels and chemicals. The pathways shown in Eq. (2.3) are overall reactions. Each of them has several elementary steps and various probable reaction mechanisms. For example, in the electrochemical conversion of CO₂ into methanol there are at least two possible reactions pathways. One mechanism involves dioxymethylene ion (HOCO⁻) and carbon monoxide (CO) as reaction intermediates, Eq. (2.4). Another mechanism proceeds through the formation of formate (HCOO⁻) and formic acid (HCOOH), Eq. (2.5). Both mechanisms involve the formation of HCO species and formaldehyde (CH₂O) [6]:



2.2 Fundamental Challenges

In addition to the thermodynamic considerations discussed above, there are also kinetic limitations. Generally speaking, it is much more challenging to convert CO₂ into highly desirable organic compounds such as formic acid and methanol than into small molecules such as CO. Formation of more complex molecules requires multiple proton-coupled electron transfers, which results in significant kinetic barriers and, therefore, low conversion efficiency. Finding a suitable catalyst that can promote formation of all intermediates simultaneously, while not catalyzing undesirable parasitic reaction is a great challenge. Such a catalyst would have to have low kinetic barriers (activation energies) for each desirable reaction step. One option could be performing different reduction steps using different catalysts, but it is much more desirable from the practical point of view to convert CO₂ into a liquid compound directly, in a single electrochemical device.

One of the fundamental challenges in the electrochemical CO₂ reduction is the high cathode overpotential (the difference between the applied electrode potential and the thermodynamic potential). The overpotential consists of three components, namely ohmic overpotential, activation overpotential and concentration overpotential. The ohmic losses are due to electrode and electrolyte resistances. The activation overpotential reflects the kinetic barrier, i.e., the energy required to

maintain the electrode reaction at a significant extent. The electrode surface can be deactivated by poisoning caused by adsorption of reaction intermediates. Therefore, selection of a proper electrode material is crucial. The concentration overpotential develops due to the mass transfer limitation caused by the diffusion of reactants and products towards/from the electrode surface. Since the electrochemical reduction of CO₂ is carried out in an aqueous medium at relatively low temperatures, the diffusion is relatively slow. If the diffusion rate of CO₂ to the electrode is significantly slower than the maximum rate of its consumption at the electrode surface, a limiting current is reached. Thus, the electrode morphology becomes a very important factor in the electrochemical cell performance. For any practical implementation, the issue of the limited mass transfer of CO₂ to the cathode surface has to be addressed.

Another intrinsic limitation is the low solubility of CO₂ in water. The CO₂ solubility in water exposed to pure CO₂ is about 30 mmol/L (at 101 kPa and 293 K). However, in aqueous electrolytes used in electrochemical reduction the CO₂ solubility is lower, due to the high ionic strength (up to 10 M). Providing a pure CO₂ stream will require pre-concentration of CO₂ containing feedstocks. This can be done by pressure swing adsorption or membrane separation, but capital and operation costs are high, which will result in a significant increase of the overall production cost. Using diluted CO₂ streams directly, without any upstream pre-concentration, is preferable. However, low CO₂ content (e.g., 10–15 mol% CO₂ in fossil fuel combustion flue gases) will result in lower concentration of the dissolved CO₂. The eventual negative outcome from the low CO₂ solubility in water and, thus, low concentration of aqueous CO₂ is the limiting current density that can be easily estimated using the following equation [2]:

$$i_L = nFk_m C_b \quad (2.6)$$

In this equation, n is the electron stoichiometry coefficient ($n = 2$), F is the Faraday constant (96485 kC/kmol), k_m is the mass transfer coefficient (10^{-5} m/s), and C_b is the bulk concentration of CO₂ (0.03 kmol/m³ for pure CO₂ at 101 kPa and 293 K). Simple computation shows that the limiting current density is $i_L = 0.06$ kA/m². For diluted CO₂ containing streams, this limiting current will be further declined. Such geometric current densities, below 0.1 kA/m², are considered as insufficient for typical industrial applications involving electrochemical processes. The economics dictate that geometric current densities above 1 kA/m² with current efficiencies of at least 50% are usually required to make the technology profitable [2]. The reason is that the rate of an electrochemical reaction per electrode area (r , mol/(m² s)) is directly proportional to the current density via Faraday's law (FE is faradaic efficiency, also called current efficiency):

$$r = \frac{R}{A} = i \frac{FE}{nF} \quad (2.7)$$

Solving this equation for A (total electrode area) gives the dependence of the required electrode area on the production rate (R , mol/s) and current density (i):

$$A = \frac{RnF}{i \times FE} \quad (2.8)$$

The above equation simply dictates that the required electrode area is inversely proportional to the current density. Therefore, for low current densities, large electrode surfaces will be required, resulting in a large size of the electrochemical device and, therefore, high capital investments and operating costs. In industrial applications, typical capital costs for electrochemical reactors are on the order of magnitude of \$10,000 m⁻² of anode or cathode area. To afford such high capital investment, electrochemical processes are typically operated with current densities of 1 kA/m² and higher, with faradaic efficiencies above 50%. On the other hand, industrial space velocities for gaseous feed have to be at least higher than 100 h⁻¹, preferably on the order of magnitude of 1000 h⁻¹ (contact times of seconds). These limitations set a challenging set of requirements for the design of an economically viable electrochemical device for the CO₂ conversion into liquid fuels and chemicals.

2.3 Catalysis for Electrochemical Reduction of CO₂

For the deployment of practical applications for the electrochemical reduction of CO₂ to liquid fuels and chemicals, highly efficient electrocatalysts have to be developed. An electrocatalyst participates in the electron transfer reaction on the electrode and facilitates the electrochemical reaction that takes place on the electrode surface, Fig. 2.2. For efficient electrocatalysis, both processes must be accelerated simultaneously. Thermodynamically, it has to be a good match between the redox potential for the electron transfer reaction and the catalyzed electrochemical reaction (reduction of CO₂). Ideally, an optimal electrocatalyst should

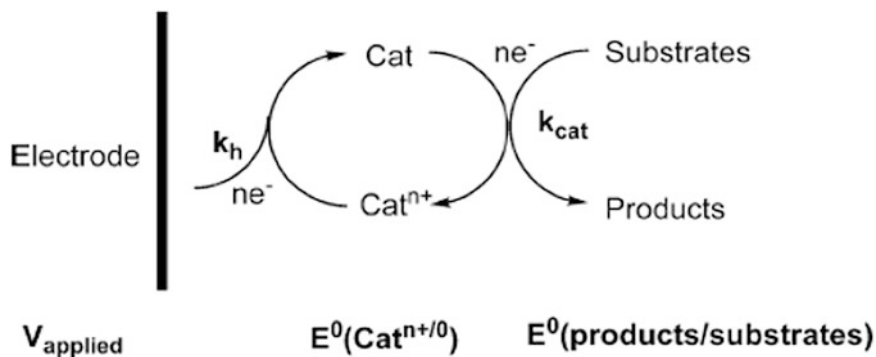


Fig. 2.2 Schematic representation of electrocatalysis in the proximity of the electrode surface with electron source [5]

operate near the thermodynamic potential of the occurring electrochemical reaction. In the search for an optimal electrocatalyst, various catalytic materials are typically screened for their redox potentials, as well as for the electron transfer rate, chemical kinetics, and current efficiencies. To identify highly efficient catalysts, all these characteristics have to be considered. Electrochemical phenomenon is quite complicated, as it involves both chemical kinetics and electrical processes.

As it was already mentioned in the previous section, direct electrochemical reduction of CO₂ on the electrode surface requires large overpotentials (the difference between the applied voltage and redox potentials of reactants and products). Large overpotentials result in low conversion efficiencies. Both thermodynamic and kinetic considerations have to be considered in order to overcome this limitation, at least to certain extent. In order to minimize the overpotential, the catalyst formal potential has to be well-matched with redox potentials of species participating in the electrochemical reaction. In addition, the reaction rate constant (k_{cat} in Fig. 2.2) and the rate constant for the electrocatalyst reduction (k_h in Fig. 2.2) must be high at the applied voltage. Common approaches for evaluation of rate constants for a given catalyst are cyclic voltammetry and rotating disk voltammetry [5].

Herein, it is useful to differentiate between *redox catalysts* and *chemical catalysts*. In redox catalysis, the catalyst is an electron transfer agent shuttling electrons between the electrode and the reactant. The chemical reaction acceleration is due to more efficient electron supply, which can be also achieved by improving the electrode morphology to make it porous as opposed to a classical flat electrode surface. In chemical catalysis, a catalyst undergoes more intimate interaction with chemical species undergoing chemical transformations. An ideal catalyst/electrode assembly would facilitate both mechanisms, significantly lowering the overpotential and the activation energy of the electrochemical reaction.

It is also necessary to distinguish between *homogeneous* and *heterogeneous catalysis*. While the electrochemical CO₂ reduction can be catalyzed either homogeneously or heterogeneously, the two approaches have different reaction mechanisms and require different electrochemical cell designs. In homogeneous catalysis, the catalyst molecules, which are dispersed in the electrolyte solution containing the substrate, diffuse to or from the electrode surface. Homogeneous catalysts for the electrochemical reduction of CO₂ are typically reduced states of transition metal complexes with macrocyclic, bipyridine or phosphine ligands [5]. In heterogeneous catalysis, the electrode material itself can act as electrocatalyst, or another catalytic material can be dispersed or immobilized on the porous electrode surface [8]. In early studies, bulk metals (e.g., Cu, Ni, Fe, Ti) were used as catalysts, employing single-element metallic electrodes in polycrystalline form. More recently, new types of heterogeneous electrocatalyst morphologies were developed, including transition metal nanoparticles, nanotubes, nanowires, core-shell structures, and nano-porous films. Homogeneous catalysts are generally less prone to deactivation since the bulk electrolyte provides a constant source of catalytic molecules replacing those that have been deactivated during each catalytic cycle. However, heterogeneous systems with the catalyst deposited or immobilized within the highly porous electrode surface have a very important advantage of compactness.

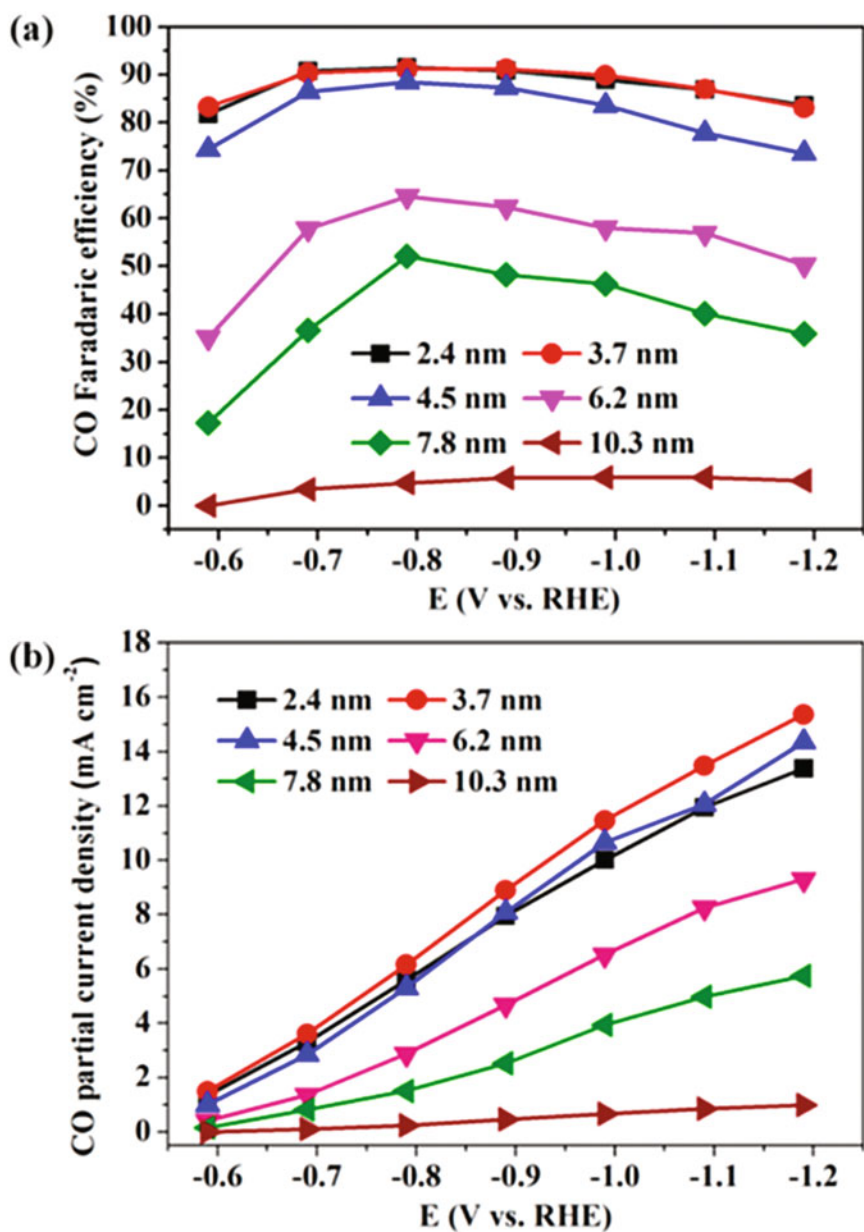


Fig. 2.3 Applied potential dependence of Faradaic efficiencies (a) and current densities for CO production over Pd nanoparticles with different sizes [9]

Among homogeneous catalysts, metal complexes such as phthalocyanine and tetraazomacrocyclic complexes of cobalt and nickel were demonstrated for the electrocatalytic reduction of CO₂ to CO, providing faradaic efficiencies of up to 98%. Rhenium and ruthenium bipyridine complexes and phosphine complexes of rhodium and palladium were also reported to be active in the electrochemical reduction of CO₂. One of the concerns regarding practical implementation of such catalysts is obviously the high cost of the catalyst that, in combination with low production density (rate of production per device volume), limits the economic viability of this approach. In heterogeneous catalysis, the use of transition metal nanoparticles as electrocatalysts is a promising avenue. The size of nanoparticles is of crucial importance because, similar to thermocatalysis, there is a strong size-activity relationship. For example, a prominent size-dependent activity and selectivity was identified in the electrocatalytic reduction of CO₂ to CO over Pd nanoparticles with sizes ranging from 2.4 to 10.3 nm [9]. Faradaic efficiencies varied from 5.8% over 10.3 nm nanoparticles to 91.2% over 3.7 nm nanoparticles, along with an 18-fold increase in current density, Fig. 2.3.

2.4 Electrochemical Cell Design

The majority of the work reported on the CO₂ electroreduction is on electrocatalysis, mainly focusing on catalytic characteristics of the electrode reactions. For such investigations, laboratory experiments are typically performed in small batch electrochemical cells under ideal conditions that do not reflect practical applications. These studies are of course of crucial importance for identification of optimal catalytic systems and understanding cathodic mass transfer limitations. However, for practical implementation, the next step has to be the design of a scaled-up, continuous flow device. So far, there is only a limited number of reports that refer to industrially feasible applications [2].

In terms of the electrochemical cell configuration, there are several conceptual options [7], Fig. 2.4. Some configurations are less suitable for the electrochemical CO₂ reduction. For example, the fuel cell-like configuration, Fig. 2.4a, could be unfavorable for CO₂ reduction due to the competing H₂ evolution reaction. To prevent the excessive flux of protons towards the cathode, a pH-buffer could be introduced, Fig. 2.4b. However, in this case the cell resistance could be too high if the buffer layer is thick. Another option is to use an anion-exchange membrane, Fig. 2.4c, simplifying the buffer-layer-based system. Yet another configuration is based on the use of a Nafion membrane in its K⁺ form, which allows the oxygen evolution reaction to be carried out in alkaline conditions and CO₂ reduction on the cathode, Fig. 2.4d. An important breakthrough was the successful implementation of gas diffusion electrodes (which are used in fuel cells) in the electrochemical cell for CO₂ electro-reduction [10], Fig. 2.5. The use of the gas diffusion electrode is a promising approach as it can improve mass transfer characteristics. However, it is

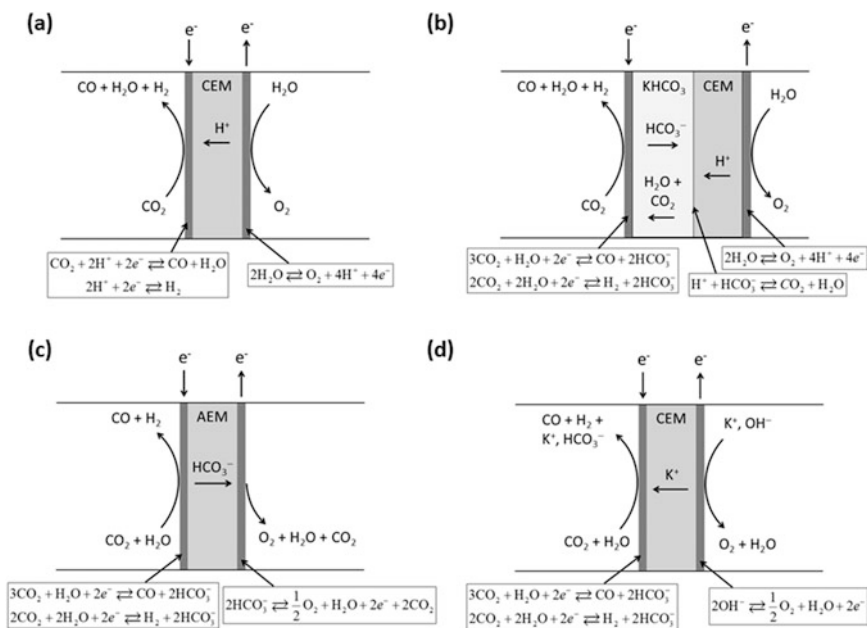


Fig. 2.4 Various designs of electrochemical cells: electrochemical cell with a cation-exchange membrane (CEM) as electrolyte (a), modified cell with a pH-buffer layer of aqueous KHCO₃ (b), electrochemical cell with an anion exchange membrane (AEM) as electrolyte (c), and electrochemical cell based on a cation-exchange membrane in the K⁺-form (d)

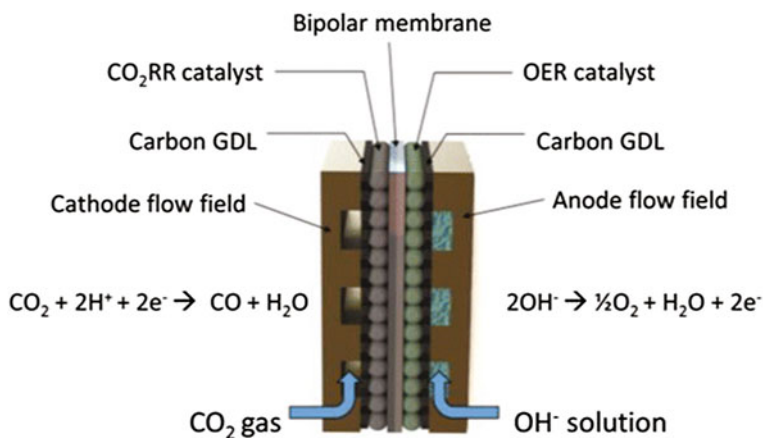


Fig. 2.5 Schematic drawing of the electrochemical device for CO₂ reduction with serpentine flow fields and gas diffusion layer (GDL) made of porous carbon paper [10]

associated with the drawback of the accumulation of liquid phase products in the gas diffusion electrode pores leading to blockage.

2.5 Methanol Synthesis

Among various approaches for CO₂ utilization, the electrochemical reduction of CO₂ appears to be an attractive alternative, since in this technology electrical energy (including renewable electricity) is used to convert CO₂ into value-added chemicals under mild conditions. This approach provides a method to recycle the emitted CO₂ creating a carbon neutral cycle and, at the same time, to store the renewable (or excess) energy from intermittent sources in the chemical energy of a synthetic fuel. There is, therefore, a significant potential to reduce our dependence on fossil fuels. Among the products which can be generated via the electrochemical reduction of CO₂, methanol is of particular interest as an important platform chemical.

Methanol has quite high energy density, which is almost half of the energy density of the gasoline (15.6 MJ/L vs. 34.2 MJ/L). In addition, methanol is also an essential intermediate for many important chemicals including paints and plastics. For the use as an energy carrier, it is beneficial to convert H₂ into methanol, which has much higher volumetric energy density than H₂ and can be stored at atmospheric pressure in liquid form. Importantly, methanol can be also directly utilized in energy converting systems such as internal combustion engines and direct methanol fuel cells. Due to the abovementioned benefits, the CO₂ electroreduction into methanol has recently gained growing attention. Yet, although significant advances have been made in this direction, more work is still required in order to develop an economically viable technology which can be commercialized on an industrial scale. Currently, most of methanol worldwide is produced in large scale industrial plants via steam reforming of natural gas to produce syngas, which is then converted to methanol in high pressure (20–30 MPa) synthesis. In contrast, the electrochemical transformation of CO₂ is performed under ambient conditions and CO₂ emitted from fossil fuel power plants and other industries can be in principle utilized. If such “methanol economy” would be implemented on large scale, it could contribute significantly to solving the problem of climate change and to reduction of our dependence on fossil fuels, Fig. 2.6 [6].

A significant progress has been made in understanding the mechanisms of the electrochemical reduction of CO₂ into methanol. The formation of methanol is known to occur heterogeneously on several electrocatalysts. Applied cathodic materials include copper (Cu), as well as its oxides and alloys with other metals, such as Ni, Sn, Pb, Zn, Ag and Cd [6]. Other electrocatalytic materials such as molybdenum (Mo) and ruthenium (Ru) are also active in the CO₂ electroreduction to methanol providing faradaic efficiencies up to 60%. Other transition metals (e.g., Fe, Ti) can be also used, as well as noble metals (Pt and Pd). Among all these materials, the oxidized Cu-based electrodes seem to be the most promising as they provide both high selectivities and current efficiencies [6].

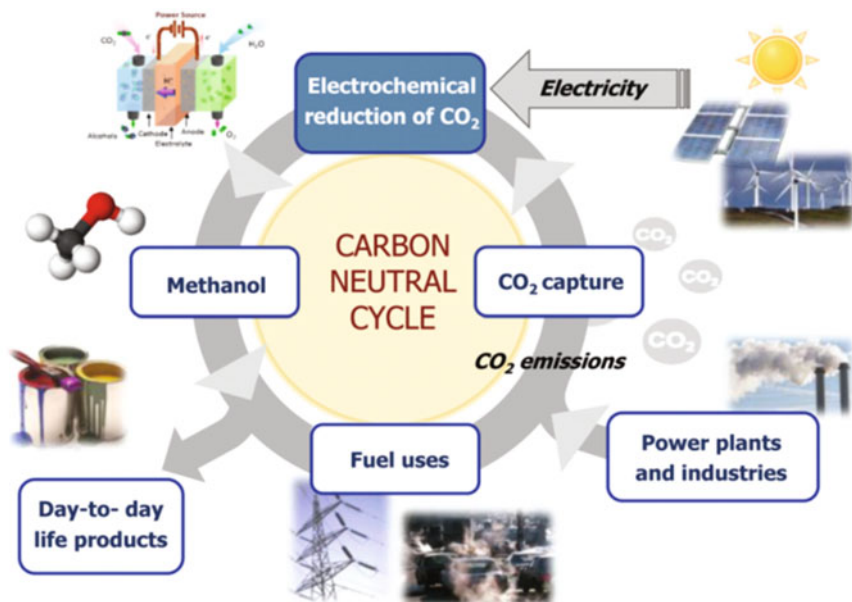


Fig. 2.6 The methanol-based economy cycle model [6]

Despite recent progress, the production of methanol via the electrochemical route is still far from its practical application. Several fundamental drawback have to be resolved in order to make this technology economically viable. First, the electrocatalyst stability at high current densities is still poor. The major problem is that reaction intermediates poison the active sites leading to fast catalyst deactivation. The development of highly stable catalysts is, therefore, among highest priorities, but these stable catalysts have to be highly active and selective to methanol production at high current densities at the same time. Second, activities and selectivities of the existing catalysts are still low. The research in this direction should focus on novel catalytic materials, still unexplored for electrochemical methanol synthesis. In addition to the catalytic material selection, the electrode morphology should be also optimized to maximize the catalytic surface per the geometric area of the electrode. This can be achieved by implementation of novel materials with high specific surface area, e.g., metal organic frameworks (MOFs). The ultimate goal is to create an optimized electrode morphology that can facilitate both electron transfer and mass transport, while having a highly active and selective catalyst that facilitates reaction rates. Finally, there is still a lot of work to be done with respect to the design of a compact and highly efficient electrochemical cell that can be scaled-up for industrial applications.

2.6 Syngas Production in Solid Oxide Fuel Cells

Fuel cells are electrochemical conversion devices that directly generate electricity by oxidizing a fuel. In a solid oxide fuel cell (SOFC), a solid oxide electrolyte is used, to differentiate from other types of fuel cells based on liquid or polymer electrolytes. There are several advantages associated with the use of SOFCs, including fuel flexibility (other than H₂ fuels can be directly used), high efficiency, long-term stability, and relatively low cost. However, due to the low electrolyte conductivity SOFCs have to be operated at high temperatures (typically 800–850 °C), which results in long start-up times and mechanical stability issues. As any other type of fuel cells, SOFCs can operate not just as a fuel cell but also as an electrolyzer [1, 11, 12]. In the fuel cell operation mode, the SOFC converts the chemical energy of a fuel into electricity through a chemical reaction. In the electrolysis mode of operation, the cell can reduce water and CO₂ into H₂ and CO, producing syngas. In this case, it is more appropriate to refer to the electrochemical cell as solid oxide electrolysis cell (SOEC), Fig. 2.7.

The advantage of the solid oxide electrolyte is that this type of electrolyte conducts oxide ions. Therefore, the SOEC can directly reduce both CO₂ and H₂O to CO and H₂. The mixture of CO and H₂ is syngas, an important chemical feedstock for the Fischer-Tropsch process and methanol synthesis. Other types of fuel cells are based on electrolytes that conduct protons (proton exchange membrane fuel cell, PEMFC), or hydroxide ions (alkaline fuel cells, AFC, or anion exchange membrane fuel cells, AEMFC). The high operation temperature of SOECs (above 800 °C) provides both thermodynamic benefit (high efficiency) and kinetic advantages (accelerating splitting of the reactants). As a result, SOECs operate with lower electricity consumption and the need for (often expensive) highly active catalysts is eliminated, as at such elevated temperatures kinetics is very fast.

In terms of practical implementation, the use of SOECs for CO₂ reduction seems as a very promising approach. In such a process, CO₂ and steam can be co-fed to an array of SOECs producing synthetic gas (syngas, a mixture of CO and H₂), Fig. 2.7. The high operating temperature allows for heat integration with other processes, such as downstream conversion of syngas into synthetic fuels and

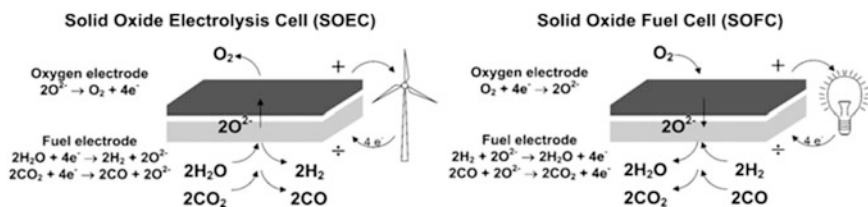


Fig. 2.7 Schematic presentation of the operational principle of a solid oxide electrolysis cell (SOEC) and a solid oxide fuel cell (SOFC) [11]

chemicals, increasing the overall efficiency. For example, the heat generated in the downstream fuel synthesis can be utilized for generation of steam fed to the SOEC. Therefore, arrays of SOECs have a potential to be implemented for high throughput production of synthetic fuels from steam and captured CO_2 , at a high efficiency, relatively low capital investment (SOECs are based on ceramic materials). The main drawback is related to mechanical instabilities of the cell materials subject to high temperatures and repeated start-up/shut-down cycles.

2.7 Concluding Remarks

The electrochemical reduction of CO_2 is an attractive avenue for converting captured CO_2 into value-added synthetic fuels and chemicals. Various sources of CO_2 can be potentially utilized, including combustion off-gases, biogas from farming, and landfill gas. Conceptually speaking, probably the most important advantage of this technology is that electricity can be directly converted into chemical energy of a synthetic compound in an electrochemical device. This energy conversion pathway allows for storing intermittent renewable or surplus electricity in the form of an easily transportable chemical feedstock, such as methanol or formic acid. In principle, it is possible to generate negative carbon footprint fuels and chemicals using solar, wind, and hydro energy, water and captured CO_2 . Among possible products of the CO_2 electroreduction, the most practical are probably methanol (used in the polymer and paint industries, can be used as a fuel), formic acid (used in the textile industry and as a preservative), and syngas (can be converted to methanol or synthetic crude via the Fischer-Tropsch process).

The potential is enormous but the challenges are difficult to overcome. First of all, there are some fundamental, intrinsic drawbacks related to the low CO_2 solubility in aqueous environments and similar redox potentials of competing reactions. These limitations can be referred to as thermodynamic in their nature, as they cannot be overcome in a classical electrochemical cell. Other issues stem from kinetic and mass transfer constraints leading to large electrode overpotentials and limiting current. Further advances are required in the CO_2 reduction electrocatalysis and electrode morphology design. However, the development of a highly active, selective, and stable catalyst and an optimized electrode morphology will not immediately lead to large-scale industrial implementation. The optimized electrode has to be incorporated in a highly efficient electrochemical cell, which has to be scalable. In addition to the mass transfer limitations near the electrode surface, there will be mass transport constraints at the level of the entire electrochemical device as well. Only once a scalable electrochemical device for the CO_2 electroreduction has been designed, the question of the economic feasibility of this technological pathway can be properly addressed.

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