Recent Technological Progress in CO₂ Electroreduction to Fuels and Energy Carriers in Aqueous Environments

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Here we review recent developments and technological advances in the field of electrochemical reduction of carbon dioxide to fuels, energy carriers and precursors and other interesting building blocks for industrial applications. Synthetic hydrocarbons derived from CO₂/H₂O are proposed as alternatives to hydrogen as an energy carrier that enables a carbon-neutral energy cycle, given their inherent advantages of high H/C ratio and convenience of storage and transportation. The electrochemical reduction of CO₂ represents a feasible route for the direct generation of hydrocarbon fuels or their precursors (i.e., synthesis gas) using CO₂/H₂O. Such hydrocarbons fit well within the existing energy infrastructure because of their similarity to existing fossil fuels. Recently significant efforts are being devoted to the development of prototype systems, such as low- or high-temperature electrolyzers that operate as part of environmentally sustainable energy networks.

1. Introduction

Current strategies to reduce atmospheric CO₂ emissions can be divided into four categories.[1–7] 1) Improvements in energy efficiency: this provides the greatest return on investment and is strongly pursued in most consumer applications.[1–3,5–8] 2) Approaches that include the use of non- or low-carbon energy sources (i.e., solar, wind, nuclear), which require significant managerial effort due to temporal variations, safety issues, and long-term waste disposal problems.[1–3,5] 3) CO₂ capture and geological sequestration (CCS), that however often conflicts with the availability of an appropriate geological medium for long-term CO₂ storage (with controlled environmental effects).[1–3,5–9] 4) A fourth category of approach focuses on CO₂ utilization, which means CO₂ conversion to a variety of useful products.[1–12] The greatest challenge concerning CO₂ utilization relates to the inherent stability of the CO₂ molecule: in fact, a lot of energy is required in any chemical transformation. Thus, the development of CO₂ utilization processes involves the minimization of the energy required for its conversion together with the utilization of energy sources that do not generate net additional CO₂ release in the process.[9,10,13]

Among a variety of conversion approaches, electrochemical methods have a number of advantages,[4–14] in particular the following aspects are noteworthy: 1) electroreduction is generally undertaken at room temperature with the possibility of minimizing chemical consumption by the recycling of electrolytic components; 2) the use of renewable energy sources (as the electricity force) to drive the conversion, which means no additional CO₂ production: from this specific viewpoint, the method can be also considered a renewable energy storage mechanism; 3) the electrochemical conversion of CO₂ can be customized to provide a preferred product by selecting suitable electrocatalysts, electrolytes, and applied voltages. In this way CO₂ can be converted electrochemically to several targeted molecules.[8] On the other hand, electrochemical reaction systems need to be compact, modular, usable on-demand, and easily scaled up.[4–14] Therefore, the exploitation of CO₂ electroreduction in the future will strongly depend on technological aspects, such as the practical design and construction of electrochemical devices, including component matching, stability, and operative conditions.[5–11] Technological and practical aspects of CO₂ electroreduction that have been developed over the last decade, together with future perspectives will represent the common thread through the individual sections of this review.

2. CO₂ Electroreduction to Fuels and Chemical Carriers: A Brief Chronological Overview

A bibliometric analysis of the scientific literature regarding CO₂ reduction,[7] for the period 1999–2009, gives a brief chronological overview of the increasing relevance of waste CO₂ reduction. Focusing on the Science Citation Index-listed periodicals from 1999 to 2009, Wan et al.[7] pointed out that a total number of 3177 authors from 56 different countries wrote 855 articles published in 355 journals within 102 different subject categories. According to Wan’s analysis, the most frequently cited paper dealt with chemical CO₂ fixation by the use of molecular-based catalysts for the coupling of CO₂ and epoxides.[7] A general theme that emerges from this literature overview is the importance of the chemical conversion...
approach to reduce waste CO₂ into useful/fine chemicals. A ranking of subject category in the same bibliometric analysis places “energy and fuels” and “electrochemistry” at positions 5th and 6th, respectively, on the basis of the number of articles and citations per publication (CPP), among a total number of 10 subjects. More recently the electrochemical reduction of carbon dioxide (ERC) has been extensively reviewed by DuBois (2006 and 2009), Gattrell (2006), Hori (2008) and Saveant (2008). Other reviews, perspectives and book chapter/essays (2010–2014) concerning the chemical recycling of CO₂ have been presented by Centi and coworkers, Saveant and coworkers, Mustain and coworkers, Saveant and coworkers, and Kubiak and coworkers. Kubiak’s group focused their overview on a photo-electrocatalysis approach. Commonly the discussion deals with the process efficiency as well as the renewable power usage to make the processes economically feasible; consequently, researchers have recognized that the biggest challenge for ERC is the poor performance of electrolyzer core components (i.e., the electrocatalysts, both in terms of catalytic activity and stability). It is well understood that ERC can proceed through two-, four-, six-, or eight-electron reduction pathways according to the specific experimental conditions. Potential products include compounds such as carbon monoxide (CO), formic acid (HCOOH), oxalic acid (H₂C₂O₄) (or the related carboxylates in alkaline environments), formaldehyde (CH₂O), methanol (CH₃OH), methane (CH₄), ethylene (C₂H₄), ethanol (CH₃CH₂OH) as well as other industrially important chemicals (i.e., acetone, hydroxyacetone, acetaldehyde, propanol, propionaldehyde, etc.) The most extensively studied electrocatalysts for ERC are based on transition metals in the form of simple metal foils, nanoparticles, nanostructured surfaces, or supported organometallic complexes. Specific properties of the different metal-based catalysts have already been reviewed in detail in 2014.

Important aspects of the ERC reaction require careful consideration. For example kinetic aspects such as reaction rates and mechanisms, combined with the thermodynamic electrochemical half-reactions and their associated standard electrode potentials. The ERC reaction involves very complicated reaction pathways and very high activation electrochemical overpotentials, even in the presence of metal electrocatalysts. Furthermore, in most cases the product selectivity is poor, as the electroreduction yields are not a single species but usually a mixture of different products. Finally, for the majority of metal-based catalysts the average catalyst life time is still far below the requirements for practical commercialization. Therefore the biggest challenges in developing ERC technology are still the practical aspects such as the electrocatalysts, electrolyzer efficiency, stability, and also the overall process costs.

Hence, while several review articles related to CO₂ reduction have already been published, a comprehensive review specifically focusing on the realization of electrolyzer prototypes, their efficiency and stability properties, and scale-up efforts is definitely important to help in improving engineering and economic feasibility for processes addressed to the conversion of CO₂ to fuels or chemical feedstock.
3. CO₂ Electrolyzers: Working Conditions

3.1 General aspects

A variety of working conditions have been investigated for ERC, including gaseous, aqueous, and non-aqueous phase techniques, at both high and low temperatures. High temperature CO₂ conversion is usually carried out using a variation of solid-oxide fuel cells (SOFCs), whereas low-temperature processes in aqueous environments largely utilize transition-metal electrodes in H⁻- or OH⁻-conducting electrolyzers.[18]

In the case of solid-oxide devices, ERC selectivity and performance often exceeds those reported for low-temperature systems, as the variety of products obtained at low temperatures is broader than those obtained under high temperature conditions.

The following section (3.2) introduces ERC solid-oxide electrolyzers and compares the advantages/disadvantages of operating at high (CO₂, CO₂ + H₂O-steam) or low (CO₂ + H₂O-liquid electrolyte) temperatures, both operating in an aqueous environment (steam, or water solution). The following sections are then dedicated to a description of low-temperature aqueous-based electrolyte devices.

3.2 Solid-oxide electrolyzers: high temperature benefits

In recent years, there has been increasing interest in H₂ as an alternative energy carrier. The majority of hydrogen is still produced directly from hydrocarbon fuels, resulting in the co-generation of CO₂. An alternative method used to produce H₂ is represented by the electrolysis of water:

Steam electrolysis

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2, \quad \Delta G = 188.7 \text{ kJ mol}^{-1} \quad (1) \]

Low-temperature H₂O electrolysis using alkaline or proton exchange membrane electrolytes has been extensively studied and represents a commercially available technology; however the process suffers from low efficiency because of the high energy demand. Therefore, solid oxide electrolysis cells (SOECs) have recently gained much interest. High operating temperatures can reduce the electrical energy requirement of the electrolysis process and, therefore, the H₂ final cost.[39]

In addition to steam electrolysis, SOECs are capable of CO₂ electrolysis. High temperature operating conditions (500–1000 °C) confer thermodynamic and kinetic benefits on the device, decreasing the electrical energy demand, charge transfer and transport overpotentials for the cathodic reduction of CO₂ to CO and O²⁻ anions. In 2008, Bidrawn et al.[39] demonstrated that CO₂ can be electrochemically reduced with an efficiency that is comparable to that which can be achieved for water electrolysis.

The co-electrolysis of CO₂ and H₂O has the potentiality to yield synthesis gas (CO + H₂) that can be further converted to liquid fuels by Fischer–Tropsch processes. The co-electrolysis process is more complicated than steam electrolysis; in fact it is not yet well understood whether CO₂ and H₂O are simultaneously electrolyzed, or whether steam is predominantly converted to H₂ or is involved in the reverse water-gas shift reaction (RWGS).

CO₂ electrolysis

\[ \text{CO}_2(g) \rightarrow \text{CO}(g) + \frac{1}{2} \text{O}_2(g), \quad \Delta G = 189.2 \text{ kJ mol}^{-1} \quad (2) \]

RWGS

\[ \text{H}_2(g) + \text{CO}_2(g) = \text{H}_2\text{O}(g) + \text{CO}(g), \quad \Delta G = 0.51 \text{ kJ mol}^{-1} \quad (3) \]

In traditional solid oxide electrolyzers (SOEs), O²⁻ anions are transferred across an oxide-ion conducting electrolyte (e.g., yttria-stabilized zirconia, YSZ) and evolves as pure O₂ on the anode side.[37]

\[ \text{O}^{2-} \rightarrow 2\text{e}^- + \frac{1}{2} \text{O}_2(g) \quad (4) \]

The operation of SOECs and SOFCs is further illustrated in Figure 1.

In the past, the reduction of CO₂ in SOEs over Pt or Pt/YSZ catalysts was used to develop an electrochemical process for pure O₂ generation (i.e., for use in NASA’s Mars Missions). Over the last decade[35,37–39] CO₂ electrolysis has been carried out mostly using Pt-free cathodes, that is, Ni/YSZ, conventionally employed in solid-oxide fuel cells (SOFCs). For example Bidrawn and coworkers investigated how Pd–ceria/La(Sr)Cr-manganite composite materials compared to Ni/YSZ.[36,40] The Pd/LSCM-based electrode showed higher performance at low operative temperature. Currently, problems associated with electrode aging by the deposition of carbon coke and/or the presence of impurities in the gas feed represents the main research challenges. In 2013, Cheng and coworkers[37] investigated process feasibility using a Ceria–Gadolinia-based electrode, that is, Cu/GDO, to reduce the performance degradation due to metal sintering/migration, carbon deposition end electrode delamination.

Figure 1. Schematic representation of a solid oxide electrolysis cell (SOEC) and a solid oxide fuel cell (SOFC). Reprinted with permission from Ref. [38], Copyright (2009), Elsevier.
significant stability improvement was observed in a time gap of 2 h of SOE–CO₂ conversion at 750 °C.

Proton-conducting solid oxide electrolyzers, as the reverse mode of proton-conducting solid oxide fuel cells, have recently attracted much attention[41] in the ERC field: this kind of device is based on the high-temperature steam electrolysis to protons at the anode (Figure 2).[41]

Protons can diffuse across the H⁺-conducting electrolyte, that is, BaCe₀.₆(Zr₀.₂Y₀.₄Zn)₀.₂O₃₋ₓ (BCZYD) to the cathode side (i.e., Fe/Fe₂O₃-BCZYD composite catalyst); where, along the triple-phase boundary, in situ CO₂ electrochemical reduction to hydrocarbons can take place, competing with both the H₂ generation and the reverse water–gas shift reaction.

Many challenges still face the implementation of SOECs. High and stable performance through the selection of suitable catalysts and components is required to reduce the production cost.

3.3 Low-temperature/aqueous-based electrolysis devices

An ion-exchange polymer electrolyte membrane (PEM) can be used to separate the anodic and cathodic compartments during CO₂ electroreduction. Many studies have been devoted to the assessment of the cathodic performance, reduction mechanism pathway, activity and stability; however the anodic processes are often neglected and experiments are carried out in three-electrode-type cells, usually with a platinum wire as counter electrode. Although this choice allows the study of catalytic performance, focusing only on the cathodic processes, it prevents the development of a complete system capable of being scaled-up into an industrial process. The two main critical aspects that have been studied are: i) the need to separate the electrodes to avoid oxygen contamination on the cathode side (H-type electrochemical cell) and hence product re-oxidation; and ii) the very high power consumption due to the high anodic overpotential and high ohmic solution resistance, that reduces the energy efficiency of the entire process. The use of ion-exchange membrane technology allows, in principle, to separate the two cell compartments while keeping the electrodes in close proximity. This technology can then: i) reduce the total electrical resistance of the system; ii) lower the total cell potential; iii) limit cell component degradation; iv) increase the energy efficiency and v) mitigate oxygen contamination among the reaction products. The electrodes can be physically assembled into a membrane–electrode assembly (MEA)[42–50] or directly deposited onto the ion-exchange membrane itself, to obtain a solid-polymer-electrolyte-catalyst (SPE).[31–56] One of the critical aspects of this type of approach is the mass transport dynamics of CO₂ (both in the gas and liquid phase), which should be dealt with through a careful development of electrocatalytic structures.[42,45]

3.3.1 Electrode surface structure

Traditional metal-based electrodes in the form of non porous foils suffer from mass-transfer limitations,[34] in particular when employed in membrane electrode assemblies and in the gas phase. Therefore, many research efforts are devoted to the design and preparation of porous three-dimensional structures able to ensure efficient mass transport dynamics. A few interesting ERC examples are summarized in the following discussion. Narayanan et al. used an In-based cathode catalyst in the form of a powder deposited onto a porous carbon paper combined with a traditional water-splitting anode (Pt/C). The two electrodes were put in contact with two different membrane types; a neutralized Nafion 115 membrane (H⁺ ions are replaced with Na⁺ ions) and an OH⁻-conducting alkaline membrane. The cathodic cell compartment was filled by an aqueous hydrogen carbonate solution saturated with CO₂. The optimal total cell potentials ranged from 1.5 to 2.5 V for current densities up to 50 mA cm⁻². Concerning the system performance, the best faradaic efficiency with respect to HCOOH production started from 80% but rapidly declined to 15–20%; Narayanan and coworkers attributed this effect to CO₂ mass transfer limitations.[45] Innocent et al. used a flow-based cell setup composed of a plate Pb cathode in contact with a Nafion 423 membrane, and a Pt water-splitting anode. A maximum stable faradaic efficiency of 60% for formate synthesis was attained at a cathodic potential of −1.6 V (vs. SCE), with mass-transfer limitations mitigated by the use of the non-static setup.[42,45]

The possibility of using mesh-based metal electrodes could enhance reactant mass transfer dynamics; Subramanian et al. developed an electrochemical flow-type reactor that employed a Pb cathode electrodeposited on a stainless-steel mesh, a IrO₂/Ta₂O₅ water-splitting anode and a Nafion-type proton-exchange membrane; the electrodes were not put in direct contact with the membrane (3 mm distance). The authors studied the effect of the catholyte (bicarbonate aqueous solution and CO₂) flow rate on the faradaic efficiency for HCOOH production in this specific device: the dependence
of the electroreduction reaction rate on the flow rate indicates that the process is mass-transfer-limited. The maximum faradaic efficiency attained was 80% at a flow rate of catholyte of 3.2 mL min−1[42].

Wu et al. utilized a Sn-based electrode under similar conditions, reaching up to 90% faradaic efficiency for formate synthesis[40].

Several authors have reported that the presence of a three-phase-boundary (gas phase–electrolyte–solid phase) increases the faradaic efficiencies and reduces kinetic limitations.[57–59]

Maeda et al.[53] studied the effect of partial and total immersion of a Au-based electrocatalyst in the cathodic aqueous solution; in particular the partially immersed electrode activities were much more strongly affected by the electrochemical surface area of the electrocatalyst when compared to the totally immersed electrode. These results agree with the hypothesis that CO2 electroreduction is also diffusion-controlled. Therefore many efforts are devoted to the development of systems capable of enhancing the three-phase boundary, for example by the use of gas diffusion layers.

The gas-phase reaction has been recently reported by Centi et al.[44] These researchers describe a nanostructured Pt-based electrocatalyst deposited onto a gas diffusion layer (GDL) and hot pressed with a Nafion-type membrane. The authors focused the study on three different types of electrocatalytic reactor, characterized by different residence times (continuous, semicontinuous, discontinuous); they also reported the complete suppression of HER (hydrogen-evolution reaction) and the total production of CO along with the gaseous and liquid products including alcohols and aldehydes. A GDL-based electrode has also been employed by Bevilaqua et al.; these authors used a Cu-phthalocyanine molecular catalyst deposited onto a carbon cloth GDL, working in gas phase and anodic alkaline environment to produce almost exclusively methane and formate. Wu et al. utilized a Sn-based electrode under similar conditions, employing a Naion SPE (solid-polymer electrolyte), in other words a catalytic membrane obtained by electrolese deposition of the metal catalyst. The metalized membrane was employed in ERC to obtain CO, ethylene and formate with stable faradaic efficiencies up to 15% at −1.5 V (vs. SCE) cathodic potential.

Another interesting possibility in terms of electrocatalyst surface structure is the direct deposition of metals onto ion-exchange membranes. Komatsu et al.[56] studied a Cu-Nafion SPE (solid-polymer electrolyte), in other words a catalytic membrane obtained by electrolese deposition of the metal catalyst. The metalized membrane was employed in ERC to obtain CO, ethylene and formate with stable faradaic efficiencies up to 15% at −1.5 V (vs. SCE) cathodic potential.

Christophe et al. studied the activity of Au–Cu alloys with different compositions deposited on different polymeric membranes reporting activities and selectivity very similar to the previous cases, with hydrocarbons being the major product for Au/Cu ratios less than 0.1, while exclusively CO was obtained for higher Au quantities.[55] Ag-based electrodes deposited on H+ exchange membranes were also studied by Hori who reported the selective production of CO and HCOOH at much higher current densities than a traditional metal plate electrode.[60]

3.3.2 Acidic or Alkaline working conditions

In aqueous conditions, ERC is strongly influenced by the activity of H+ ions in solution. In particular the pH influences both the hydrogen evolution reaction (HER) and the CO2 equilibrium activity; strongly alkaline conditions (pH > 10) tend to reduce the equilibrium activity of CO2 in solution, thus reducing the reaction kinetics of the ERC and the faradaic efficiency with respect to the HER, since the reaction occurs only on free CO2 dissolved in solution.[64] however, acidic conditions tend to promote the competing HER.

Observing the thermodynamic pH-potential diagram (Pourbaix diagram) for the CO2/H2O system (Figure 3) it is
clear that the CO\textsubscript{2} reaction overlaps strongly the HER, so it is necessary to carefully assess the effect of the pH on the reaction. In addition, the reaction is influenced by the local CO\textsubscript{2} concentration and by the local pH at the electrode; both the HER and ERC generate OH\textsuperscript{−} at the catalyst–solution interface, influencing the local pH and CO\textsubscript{2} concentration. Buffer solutions do mitigate the conversion of CO\textsubscript{2} into HCO\textsubscript{3}\textsuperscript{−} (inactive for the hydrogen evolution reaction) by neutralizing the OH\textsuperscript{−} produced at the cathode.

The use of an ion-exchange membrane, by supplying H\textsuperscript{+} (acidic membrane) or removing OH\textsuperscript{−} (alkaline membrane), in combination with a buffer electrolyte limits the pH drifting of the solution. Many studies have reported the use of ion-exchange membranes, in acidic, neutral, or even alkaline conditions.

Some authors report the enhancement of the faradaic efficiency of CO\textsubscript{2} production by using a KHCO\textsubscript{3} buffer layer in a Nafion-based setup with a Ag–GDL cathode electrocatalyst. This effect was attributed to the stabilization of the pH of bulk and interface, limiting both the conversion of free CO\textsubscript{2} to HCO\textsubscript{3}\textsuperscript{−} and the HER.\cite{45–48}

Similar experiments were conducted on a Pb electrode in alkaline conditions using NaOH\cite{69} and a phosphate buffer\cite{49} as anolyte for the production of HCOO\textsuperscript{−} to demonstrate the effect of local pH.

Regarding hydrocarbon production, Hori et al. studied the CO\textsubscript{2} electroreduction on Cu sheets in a two-compartment cell separated by a cation-exchange membrane. The faradaic efficiencies and product distribution were strongly dependent on the pH and on the catholyte composition employed. When a phosphate buffer was employed as catholyte, total faradaic efficiencies ranging from 10% to 20% were attained, with the process yielding almost exclusively methane. The use of a potassium hydrogen carbonate-based catholyte increased the faradaic efficiency up to 35% at low current densities, yielding also ethylene and ethanol along with methane. Increasing the pH by using KOH suppressed methane production, while ethylene and ethanol were the only detectable reaction products.\cite{41,45}

In conclusion the overall pH and also transient pH values can strongly influence the ERC in thermodynamic terms, kinetics, and also mass transport. The pH influences the solubility of CO\textsubscript{2} and hence its mass transport aspects; in addition, since the electroreduction reactions involve one or more protons, the reaction kinetics are also influenced. Acidic conditions tend to enhance product yields, but also promote the competing HER. Strongly alkaline conditions tend to convert CO\textsubscript{2} into carbonates or bicarbonates. Although slow, this reaction is able to reduce the CO\textsubscript{2} mass transport, reducing at the same time the current efficiency. Neutral and/or in particular buffered solutions represent a tradeoff between these conditions.

### 3.3.3 CO\textsubscript{2} pressure effect in gas phase working conditions

As stated previously, the CO\textsubscript{2} electroreduction reaction is a diffusion-controlled reaction, therefore the CO\textsubscript{2} bulk and interface concentrations severely affect the entire process. Several methods have been used to enhance CO\textsubscript{2} dissolution, the most commonly used are: i) the use of a non-aqueous solvent; ii) low-temperature working conditions that lead to a decrease of the Henry constant; iii) the increase of CO\textsubscript{2} partial pressure both in liquid and in gas phases. In particular the pressure variable has a very strong effect on the ERC affecting not only the solubility of the CO\textsubscript{2} but also the thermodynamics of the process.\cite{60} Some metals like Pt or Ni are completely inactive for ERC at atmospheric pressure but can produce CO or formate under elevated pressure conditions.\cite{14,67,68}

Nakagawa and coworkers studied the CO\textsubscript{2} electroreduction reaction carried out on VIII-group metals at atmospheric and higher pressure values (50–60 bar) and reported a remarkable increase in the faradaic efficiency in the latter cases.\cite{69} Many metals with scarce activity at ambient pressure are able to successfully reduce CO\textsubscript{2} to CO, HCOOH, and even hydrocarbons at higher pressures.\cite{70} The selectivity of the products is also influenced by the CO\textsubscript{2} working pressure. Hara et al. reported about a Pt-GDL electrocatalyst able to reduce CO\textsubscript{2} mainly to methane, formate, CO and alcohols when sufficient CO\textsubscript{2} supply was guaranteed to the electrocatalysts.\cite{70} In addition, some authors report the formation of higher carboxylic acids when the reaction is carried out under elevated pressure on Pb, Ni, Hg electrocatalysts.\cite{14}

Literature considerations enable the classification of metal electrocatalysts into four different groups, according to the CO\textsubscript{2} electroreduction activity–pressure dependence:

1. Elements that exhibit scarce CO\textsubscript{2} electroreduction activity both at atmospheric and high pressure: Ti, Nb, Ta, Mo, Mn, and Al.
2. Elements that exhibit scarce activity at atmospheric pressure but able to synthesize products from CO\textsubscript{2} electroreduction at higher pressures: Zr, Cr, W, Fe, Co, Rh, Ir, Ni, Pd, Pt, C, and Si.
3. Elements able to reduce CO\textsubscript{2} to formate both at atmospheric and high pressures: Ag, Au, Zn, In, Sn, Pb and Bi.
4. Elements able to synthesize hydrocarbons, formate and CO, with variable selectivity depending on the CO\textsubscript{2} pressure working environment: Cu.

The case of Cu is one of the most challenging: higher pressures favor the synthesis of products with a higher ratio between CO\textsubscript{2} consumed molecules/exchanged-electrons. Hara et al. reported that the product distribution on copper electrocatalysts varied with increasing pressures: from hydrogen to hydrocarbons and finally to CO and formate (Figure 4). Higher pressures (current densities lower than the CO\textsubscript{2} diffusion limit) tend to favor products with the highest CO\textsubscript{2} consumed/exchanged electron ratio, since there is plenty of CO\textsubscript{2} available for the reaction; in contrast, lower pressures tend to favor H\textsubscript{2} evolution and hydrocarbon production, since the CO\textsubscript{2} available at the electrode interface decreases.\cite{71} In addition, stirring the solution favors the synthesis of products with a lower ratio of consumed CO\textsubscript{2} molecules to exchanged...
electrons (i.e., CO and HCOOH), further confirming that mass transport plays a fundamental role in ERC.

4. Laboratory-/Bench-Scale Prototypes Operating in Aqueous Environment

No standard experimental setup or methodology for studying ERC currently exists. Different laboratories have used a variety of electrolyzers or flow cells operating in aqueous environment. An overview of the representative lab-scale prototypes is reported in this section.

4.1 H-type cells and fixed-bed reactors

The most commonly used lab-scale prototypes used in ERC studies are described as H-type cells with metal plate electrodes. The H-type reactor is a divided electrochemical cell; indeed the name comes from the typical “H” form and it consists of two compartments connected through a diaphragm. This setup ensures ionic conductivity through the cell parts yet preventing the oxidation of the CO₂ cathodic products on the anode electrocatalyst and preventing oxygen contamination (produced by anodic water oxidation) in the cathodic compartment. A variety of lab applications are described in literature. [72–74]

A representative example of H-type cell, focusing on cathode catalyst investigation, was described in 2001 by Lee and coworkers [72] (Figure 5). The anodic and cathodic cell compartments were separated through an anion-exchange polymer membrane (i.e., CMX, Tokuyama Corp.). The working electrode, a Cu catalyst electrodeposited on a Pt quartz crystal, was immersed in the electrolyte static solution composed of KHCO₃ in water (cathode compartment). A carbon plate was used as counter electrode and placed in the anode compartment. This standard H-cell setup was integrated with an in situ electrochemical quartz crystal microbalance (EQCM) that enabled the investigation of the cathode electrode mass changes during the ERC. [72]

More recently, many research groups have investigated cathode properties by the use of an H-cell with the cathode compartment directly connected to a MS or GC spectrometer for product detection. [73,74]

The electrochemical fixed-bed reactor [75,76] (Figure 6) represents a different investigation platform focused on extending the electrode surface as much as possible, within a reduced cell volume. The fixed-bed reactor, in fact, allows testing of ERC electrocatalysts in the form of powders or granules, constituting the catalyst bed. In a study reported by Köleli and coworkers, the fixed-bed reactor consisted of a unique-compartment glass cell with a gas inlet placed on...
the use of gas diffusion electrodes (GDEs) for a better control of the three-phase boundary in which reactions take place. Furthermore, the versatility of the microfluidic platform enables the rapid investigation of the ERC catalyst under different operating conditions (i.e., composition and pH of the liquid electrolyte). A graphite current collector with a window allowing the flow of gases is backed on each side. A Pt counter electrode was placed directly above the electrode bed.

In 2003, Köleli and coworkers for the first time in the literature, demonstrated CO₂ conversion to formic acid (HCOOH) on Sn granules in an undivided fixed-bed reactor, at ambient conditions and in an aqueous K₂CO₃ electrolyte.[56]

### 4.2 Microfluidic flow cells and continuous flow reactors

Various laboratories have recently used the so called microfluidic flow reactor to test electrode performance in the ERC process. This type of setup consists of two electrodes separated by a flowing liquid electrolyte and it can be used to test both the anode and cathode performance (half-cell reactions) by the use of an external reference electrode.

A representative example of a microfluidic flow cell was described in 2010 by Whipple et al.[77a] and more recently by Wang et al.[78a] (Figure 7). Specifically, their device includes the use of gas diffusion electrodes (GDEs) for a better control of the three-phase boundary in which reactions take place. Furthermore, the versatility of the microfluidic platform enables the rapid investigation of the ERC catalyst under different operating conditions (i.e., composition and pH of the liquid electrolyte). A graphite current collector with a window allowing the flow of gases is backed on each GDE. Behind the cathode a PMMA (poly(methyl methacrylate)) chamber was placed for CO₂ to flow through, while the anode was left open to air for oxygen to evolve. Tin was used as cathode catalyst for the most part of the study and the corresponding production of formic acid was transported out of the reactor with the electrolyte stream; therefore the continuous flow operation makes online product collection simple and quick.

Different versions of the flow reactor have been described by Oloman et al.[60,78] Alvarez-Guerra et al.[79] Kuhl et al.[23] Lee and coworkers.[49] Innocent and coworkers.[45] The basic concept is included in the filter-press or parallel-plate type electrochemical cell (Figure 8). Notably, the cell is composed of two compartments (anodic and cathodic) separated by a proton-conducting (that is, Nafion 117)[49] or an anion-exchange membrane (i.e., Selemion AMV, AGC Inc.)[23].

In both cases, the electrochemical experiments can be undertaken in the continuous mode: two tanks serve as the reservoirs for the circulated catholyte and anolyte in their own compartment. The co-current flow of reactant composed by CO₂ plus N₂ gas and a liquid catholyte (an aqueous solution of KHCO₃) is introduced by Li and Oloman[60] to give the co-current upward two-phase (g₂l/ ᵐ) flow. The major problem of this setup is attributed to the two-phase fluid distribution through the cathode matrix; this problem even more critical when the system must be scaled up.

### 4.3 Polymer-electrolyte membrane electrolyzers

Cell configurations based on a solid polymer ion-conducting membrane electrode assembly (MEAs) with supported catalytic electrodes have a number of advantages, and these benefits are well-recognized in fuel cells. The main advantages of the MEA-based electrolysis system are, compared to single compartment systems such as single compartment reactors or microfluidic cells, the possibility to separate the two compartments, preventing the contamination of the electrodes with products derived from the opposing electrode, while keeping the electrodes in close proximity; this allows a strong reduction of the ohmic resistance, leading to net improvements in the energy efficiency of the system. The energy consumption of the process is of primary importance in practical systems but is usually neglected in research-scale prototypes. Concerning the use of polymer electrolyte-based CO₂ electrolysis cells, there exists an early technical report[40] from United States Technologies Corp.; otherwise, the use of a MEA cell configuration in CO₂ reduction has been investigated only recently.

Delacourt et al. (2008)[41] realized an electrolysis cell designed for the simultaneous electrochemical conversion of CO₂ to syngas at room temperature. The device concept was based on a technology very close to that of proton-exchange-membrane fuel cells (PEMFC), with the insertion of a pH-buffer layer (aqueous KHCO₃) between the Ag-based cathode catalyst layer and the classical proton-exchange membrane, (Nafion type). A similar concept was adopted in 2013/2014 by Wu et al.[46,49] for HCOOH production (Figure 9).

Narayanan et al. (2011)[49] extended the CO₂ conversion process to formate in a polymer electrolyte membrane cell, using an alkaline ion-exchange membrane included in the MEA. Among the different types of alkaline ion-exchange membranes, the use of the OH⁻ conducting type (i.e., AMI 700-1S, American Membrane International Inc.) in conjunction with sodium hydrogen carbonate solutions was found to be beneficial for the device efficiency. The authors pointed out different advantages to the use of an anion-exchange membrane configuration, mainly in terms of the ability to keep the products from CO₂ reduction from being re-oxidized at the oxygen electrode and the opportunity to use non-precious metal catalysts.

In 2014 Bevilacqua et al.[49] described the realization of an anion-exchange MEA electrolyzer, which combines the ERC process at the cathode with ethanol electro-oxidation at the...
anode, leading to the contemporaneous production of hydrocarbons and chemicals. The specific device was called a depolarized anode alkaline membrane CO$_2$ electrolyzer (DAAM-CE) (Figure 10).

Unlike traditional electrolyzers in which water is electrooxidized to oxygen on the anode side, the DAAM-CE drives the oxidation reaction selectively towards the formation of a value-added product such as carboxylates from alcohols. At the same time this also guarantees a much lower working cell potential than existing architectures. Under these conditions materials such as mem-

Figure 8. Upper: Scheme of the filter-press electrochemical cell. Lower: cell diagram representation of the experimental set-up. Reprinted with permission from Ref. [79], Copyright 2012, Elsevier.

Figure 9. A schematic representation of the full electrochemical cell including a buffer layer with circulating liquid electrolyte. Reproduced with permission from Ref. [48b], Copyright 2013, the Royal Chemical Society.
branes and electrocatalysts can have long term stability. The development of CO$_2$ electrolyzers such as the DAAM-CE, which work under realistic conditions of potential and current density, could ultimately contribute to the realization of large-scale processes for the abatement and valuation of CO$_2$.

Figure 10 shows a schematic representation (A) of the DAAM-CE and a photograph of the actual device (B). A GDE modified by copper phthalocyanine (CuPc@GDE) was used as cathode, while the anode electrocatalyst consists of Pd nanoparticles supported on a titanium-sintered web substrate (Pd@Ti) and the anion exchange membrane was a commercial material (Tokuyama A201). The MEA was pressed between two conductive plates on the cathode and anode sides, respectively. The cathode compartment was directly connected to a mass spectrometer for the detection of the gaseous products (e.g., CH$_4$, C$_2$H$_4$, and H$_2$) obtained by continuous electrolysis. The major hydrocarbon product detected in the cathode gas phase exhaust was methane and a continuous increase in CH$_4$ production was observed up to -1.75 V. Electrolysis tests of 6 h were performed showing a constant methane evolution during the whole experiment.

5. Scale-Up Efforts: Representative Examples for Different Selectivity Conversion

The feasibility of a process to be applied on an industrial level usual involves problems of scalability. Scale-up is usually accomplished by properly up-dimensioning the process and the boundary conditions while retaining or improving the original reaction efficiency and selectivity. Furthermore, scale-up must accomplish the task of improving the energy efficiency of the entire cycle. Here we describe scale-up efforts that can be found in the literature for different CO$_2$ electroreduction processes.

5.1 Scale-up of a continuous flow reactor

In Section 4.2 we discussed the concept of a filter-press or parallel-plate type electrochemical cell as the main example of a flow reactor lab-scale prototype, described and adopted by a number of researchers (Figure 9). Among them, Li and Oloman$^{[81]}$ extended that concept to later report experimental and modeling work for the scale-up of their continuous “trickle bed” reactor, still based on a single cell with a co-current 2-phase flow of catholyte (aqueous solution and CO$_2$ gas). The extended electrolyzer was a seven-fold scale-up from the previous one (320 vs. 45 cm$^2$), while maintaining many similarities in terms of geometrical, thermal and electrical features. Electrical consistency was insured between the small and large reactor by the adoption of the same inter-electrode gap and electrode thickness, to maintain comparable potential and current distributions between the lab-scale and scale-up prototypes. The use of a granule Sn cathode in alkaline media drove the electroreduction of CO$_2$ selectively to HCOO$^-$.

Operating with inlet CO$_2$ gas pressure up to 600 kPa and an outlet temperature of ca. 50 $^\circ$C, using 0.5m KHCO$_3$ + 2m KCl as catholyte and 2m KOH as anolyte, the scale-up reactor lead to a formate current efficiency between 63 to 91% under the same range of electrode voltage used in the lab-prototype (2.7–4.3 V). According to the authors, the next step should involve an increase in the electrode stability under working conditions and to reduce formate cross-over by optimizing the reactor design.
5.2 Scale-up for hydrocarbon production

The Research Institute Omnidea (a Portuguese small-to-medium enterprise, SME, within the European Space Agency, ESA) has recently presented the development of a technology based upon a regenerative energy storage cycle\(^\text{[82]}\) (Figure 11). In this cycle the recharge system converts CO\(_2\) to hydrocarbons (i.e., CH\(_4\), C\(_2\)H\(_4\)), by using a Cu-based cathode and a renewable power source. Furthermore the discharge system produces electrical energy when hydrocarbons and O\(_2\) products are directly supplied to a SOFC device.

The authors describe the research issues followed to bring this technology closer to the market. The main challenge is still the development of a device capable of reducing waste CO\(_2\) to hydrocarbons, without forcing the working cathodic potential to significantly more negative values. By controlling the copper electrodeposition, mainly in terms of surface area, C\(_2\) products (i.e., C\(_2\)H\(_4\), C\(_2\)H\(_6\)) can be selectively produced, with the consequent increase in volumetric energy density. A stable hydrocarbon flow for an extended time of 4 h was demonstrated by the use of the prototype device.

5.3 Pilot project from a subsidiary of Mantra Group: combining formate production from ECR to feed a mixed-reactant fuel cell

Recently,\(^\text{[83]}\) Mantra Energy Alternatives announced the deployment of a power plant that includes the ERC process. This innovative technology involves multiple consecutive steps, starting from the capture of CO\(_2\) emitted from a cement production plant. The obtained CO\(_2\) gas is purified before being fed to the ERC reactor. Formic acid or formate salts, such as potassium formate, are expected to be obtained by the use of a Sn-based electrode, but different electrocatalysts can be used to create different products.

Notably, HCOOH and HCOO\(^-\) can be used as fuel to feed a mixed-reactant fuel cell (MRFC); in this versatile fuel cell type, also licensed by Mantra Corp.,\(^\text{[84a,b]}\) a mixture of fuel and oxidant flows through the membrane-free cell as a single stream; the mixed-feed concept allows for a wide range of different cell stack designs, such as the Swiss-roll MRFC construction previously described by Aziznia, Oloman and Gyenge.\(^\text{[85,86]}\)

Finally, HCOOH/HCOO\(^-\) products can also be used in the manufacturing industry as building block for different kind of materials, such as rubber, pharmaceuticals, etc.

In the near future Mantra’s pilot plant is expected to convert 100 kg day\(^{-1}\) of waste CO\(_2\) to formate salt.\(^\text{[83]}\)

6. Light-Assisted CO\(_2\) Electroreduction

Among the various electrochemical strategies for CO\(_2\) recycling, light-assisted ERC is an interesting example and therefore deserves to be discussed in a separated section.

Artificial photosynthesis is often defined by the use of light to split water, evolving H\(_2\) as a fuel.\(^\text{[87–91]}\) The interest in generating liquid solar derived fuels has grown rapidly due to a number of advantages such as their enhanced energy density and improved storage properties.

Several approaches have been employed in the development of light-assisted ERC processes using illuminated semiconductor electrodes, both as photoanodes to supply electrons to a dark cathode, or with photocathodes to reduce directly CO\(_2\). A few interesting applications are described here.

In 2012 Panasonic developed an artificial photosynthesis system that converts CO\(_2\) to formic acid at a world record top efficiency of 0.2% by the use of an \(n\)-GaN photoanode to drive an In-based photocathode. The efficiency is on a comparable level to real plants used to produce biomass energy. The key feature of the system is the application of a nitride semiconductor which makes the setup simple and efficient. In previous approaches, systems have utilized very complex structures such as organic complexes or plural photo-electrodes, which makes it difficult to improve their efficiency in response to light. Panasonic’s artificial photosynthesis system has a simple structure that can utilize direct sunlight or focused light. Nitride semiconductors have attracted attention for their potential applications in highly efficient optical and power devices for energy saving. However, its potential was revealed to extend beyond solid devices; more specifically, it can be used as a photo-electrode for CO\(_2\) reduction. Making a structured electrode through the thin film process for semiconductors, the performance as a photo-electrode has highly improved. The CO\(_2\) reduction takes place on a metal catalyst at the opposite side of the nitride semiconductor photo-electrode. The metal catalyst plays an important role in selectively accelerating the reaction.

![Figure 11. Representative diagram of energy storage cycle technology.](image)
As noted by Bocarsly and coworkers,[91] the long term stability of the above-mentioned system was not examined. Similar III–V n-type semiconductors tend to degrade in aqueous environments, limiting their long term applicability.

6.1 Photovoltaic–electrochemical systems (PV–EC)

An interesting alternative to photoelectrochemical systems is the use of an external photovoltaic (PV) array that powers an electrolyzer based on metallic electrodes (coupled photovoltaic-photoelectrochemical systems, PV-EC).

Very recently (2014), the research group of Bocarsly[91] investigated the chemical output and efficiency of a coupled PV-EC system composed of a silicon photovoltaic solar array and an indium cathode-based electrochemical flow system, consisting of a 3-cell stack, capable to convert CO₂ to HCOOH (Figure 12). The coupling of independent PV and PEC units enables complex chemical process to be carried out, involving the multi-electron reduction of CO₂. Furthermore, PEC metal-based electrodes could allow a higher degree of scalability in terms of electrode area and multiple-cell stack design.

The storage of solar energy as formic acid, generated electrochemically from CO₂, has been identified by many authors as a viable renewable fuel pathway. Bocarsly and coworkers described the possibility to accomplish this transformation by separating light absorption and CO₂ conversion through the use of a commercial solar panel, illuminated with natural sunlight, to power a closed-loop flow electrolyzer. By the use of Sn-based cathodes this specific lab-scale prototype demonstrated faradaic yields of up to 67% for selective formate production.

7. Perspectives

In this review, we have summarized recent advances in the development of ERC processes in aqueous environments. This investigation has been focused mainly on describing technical aspects, including electrode structures, acidic or alkaline working conditions, and the effect of other working parameters (such as pressure, electrolyte concentration, etc.) related to specific application in an electrolytic cell/electrolyzer.

In many of the available literature reports, authors describe the variables affecting ERC performance by investigating the results obtained in lab-scale half-cell reactors in both semi-continuous and continuous mode; this experimental setup is considered a useful tool to preliminarily understand electrocatalyst performance under selected working conditions. The next step in ERC development has been the design and characterization of complete-cell reactors; their analysis needs to take into account an extended number of key factors, in particular component mismatch. Here we have taken care to describe in more detail the limited number of examples of complete electrolysis cells. In our opinion, the design and realization of novel ERC electrocatalysts, combined with a careful evaluation of engineering aspects including electrode structure and cell construction, represent the important elements for the next step in the improvement of CO₂ reduction to fuels, energy carriers and chemical building blocks.

8. Appendix

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>DAAM-CE</td>
<td>depolarized anode alkaline membrane</td>
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<tr>
<td>CO₂ electrolyzer</td>
<td></td>
</tr>
<tr>
<td>ERC</td>
<td>electrochemical reduction of carbon dioxide</td>
</tr>
<tr>
<td>ESA</td>
<td>European Space Agency</td>
</tr>
<tr>
<td>GDE</td>
<td>gas diffusion electrode</td>
</tr>
<tr>
<td>GDL</td>
<td>gas diffusion layer</td>
</tr>
<tr>
<td>EQCM</td>
<td>electrochemical quartz crystal microbalance</td>
</tr>
<tr>
<td>HER</td>
<td>hydrogen-evolution reaction</td>
</tr>
<tr>
<td>MEA</td>
<td>membrane-electrode assembly</td>
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<tr>
<td>MRFC</td>
<td>mixed-reactant fuel cell</td>
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</table>

Figure 12. Electrical schematic diagram for the integrated PV-stack system. Reprinted with permission from Ref. [91], Copyright 2014, Elsevier.
Keywords: carbon dioxide electroreduction · electrochemistry · electrolysis · energy conversion · green chemistry

Acknowledgements

We gratefully acknowledge the financial support from MIUR (Italy) for the FIRB 2010–Project Number RBFR10J4H7 and the Ente Cassa di Risparmio di Firenze for the project HYDROLAB2.

Energy Technol. 2000, 00, 1 – 15
Reducing CO₂: Synthetic hydrocarbon fuels derived from CO₂/H₂O are proposed as alternatives to hydrogen as an energy carrier that enables a carbon-neutral energy cycle. The electrochemical reduction of CO₂ represents a feasible route for the direct generation of hydrocarbon fuels or their precursors (i.e., synthesis gas). Such hydrocarbons fit well within the existing energy infrastructure because of their similarity to existing fossil fuels.