

Electrochemical conversion of CO₂ to useful chemicals: current status, remaining challenges, and future opportunities

Huei-Ru “Molly” Jhong^{1,3}, Sichao Ma^{2,3} and Paul JA Kenis^{1,3}

The rise of atmospheric CO₂ levels must be slowed, or better reverted, to avoid further undesirable climate change. Electrochemical reduction of CO₂ into value-added chemicals using renewable energy is one approach to help address this problem as it will recycle ‘spent’ CO₂ (carbon neutral cycle) and it provides a method to store or utilize otherwise wasted excess renewable energy from intermittent sources, both reducing our dependence on fossil fuels. Current electrolysis cells accomplish either high Faradaic efficiency (often >95% selectivity) for a desired product (e.g. CO), or reasonable current density (conversion), whereas both need to be high for a commercial process. This review will discuss current status and opportunities for catalyst design, electrolyte choice, and electrode structure.

Addresses

¹ Department of Chemical & Biomolecular Engineering, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Urbana, IL 61801, USA

² Department of Chemistry, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Urbana, IL 61801, USA

³ International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, Japan

Corresponding author: Kenis, Paul JA (kenis@illinois.edu)

Current Opinion in Chemical Engineering 2013, 2:191–199

This review comes from a themed issue on **Nanotechnology**

Edited by **Hong Yang** and **Hua Chun Zeng**

For a complete overview see the [Issue](#) and the [Editorial](#)

2211-3398/\$ – see front matter, © 2013 Elsevier Ltd. All rights reserved.

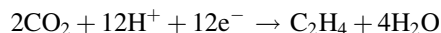
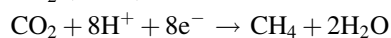
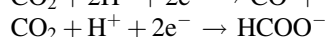
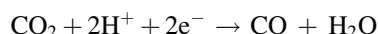
<http://dx.doi.org/10.1016/j.coche.2013.03.005>

Introduction

Carbon dioxide (CO₂) emissions into the atmosphere will need to be drastically reduced to curb the various undesirable effects of climate change. One approach is to switch from fossil fuel burning power plants to renewable sources like solar, wind, and water, which has the added benefit that we reduce our dependency on dwindling global supplies of fossil fuels. However, because of their intermittent nature, the fraction of energy that can be supplied from renewable sources will be limited to 30%, unless approaches for large scale energy storage become available. Alternatively, CO₂ could be captured from point sources such as power plants, followed by conversion into chemicals of economic value [1–3]. Potential products include formic acid [4^{••},5], methanol, CO

[4^{••},6,7[•],8–12,13^{••}], and ethylene [4^{••},14[•]] which can be formed using processes such as homogeneous catalysis [15,16], heterogeneous catalysis [17^{••},18], photocatalysis [19], photoreduction [19], or electrochemical reduction — the topic of this review. In addition to reducing greenhouse gas emissions, CO₂ conversion processes will reduce our dependency on fossil fuels for chemical synthesis. At this point, however, it is unclear which of these strategies are technologically feasible and make economic and practical sense [1]. Electrochemical CO₂ reduction has the advantage that it may be an approach to utilize excess energy from intermittent renewable sources in lieu of large scale energy storage.

This review will summarize the current status, remaining challenges, and future opportunities for electrochemical conversion of CO₂ into value-added chemicals or intermediates at low temperatures. Prior reviews and reports have provided an excellent overview of possible products of electrochemical CO₂ reduction, including CO, formate, methane, ethylene, ethanol, n-propanol, allyl alcohol, acetaldehyde, propionaldehyde, acetate, methanol, ethylene glycol, glycolaldehyde, hydroxyacetone, acetone, and glyoxal [14[•],17^{••},20]. In an electrolyzer CO₂ is reduced on the cathode while the oxygen evolution reaction (OER) takes place on the anode. Half-reactions of the cathode for electrochemical CO₂ reduction into major products such as CO, formate, methane, and ethylene are listed below.



The process of CO₂ electrolysis is basically running a fuel cell in reverse; so indeed, many lessons learned over the last five or so decades in the development of catalysts, electrodes and cell configurations of fuel cells do apply also to the development of efficient CO₂ electrolysis processes, but certain aspects will be very different and will require different optimization strategies. For example, both low-temperature fuel cells and CO₂ electrolysis cells are often limited by cathode performance, so both seek to improve slow cathode kinetics by developing more active catalysts. However, in addition to activity, the catalyst for CO₂ reduction needs to exhibit high product selectivity so the formation of desired products is heavily favored while suppressing unwanted reactions. Moreover, effective removal of products from the catalyst layer to

avoid blocking active sites is important in both fuel cells and CO₂ electrolysis cells, but the technical strategies to do so can be very different due to the different nature of products. Specifically, the oxygen reduction reaction in acidic fuel cells generates water which often leads to water management issues, whereas the CO₂ reduction reaction in CO₂ electrolysis cells often leads to the formation of both gaseous (e.g. CO, H₂) and liquid products and thus effective gas/liquid phase separation is vital. The subsequent sections will briefly review the technological requirements for catalysts, electrodes, electrolytes, and cell configurations.

Terminology and figures of merit

For electrochemical reduction of CO₂ to be performed in an efficient manner, highly active and durable electrocatalysts for both the cathode (CO₂ reduction reaction) and the anode (O₂ evolution reaction), as well as electrodes and electrolytes that have high conductivity and allow for sufficient mass transport of the reactants and products to/from the catalyst layers are required. Key figures of merit of the process that characterize its performance and thus assist in determining its economic feasibility are: (i) the *energetic efficiency* (EE) — a measure of the overall energy utilization toward the desired product; (ii) the *current density* (CD) — a measure of the rate of conversion; (iii) the *Faradaic efficiency* (FE) — a measure of the selectivity of the process for a given product; (iv) the *catalyst stability*; and (v) *process costs* [21[•]] — including material consumption costs, capital cost and electricity cost. In this review, we will focus on the first three figures of merit (EE, FE, and CD) because currently neither standard protocols for durability tests of catalysts nor cost models for major products exist for electrochemical CO₂ conversion.

The energetic efficiency can be calculated using Eq. (1):

$$\varepsilon_{\text{energetic}} = \sum_k \frac{E_k^0 \varepsilon_{k,\text{Faradaic}}}{E_k^0 + \eta} \quad (1)$$

where E_k^0 is the equilibrium cell potential for a certain product. For example, $E^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = -0.10 \text{ V} - 1.23 \text{ V} = -1.33 \text{ V}$ for converting CO₂ to CO and $E^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = 0 \text{ V} - 1.23 \text{ V} = -1.23 \text{ V}$ for H₂ evolution). $\varepsilon_{k,\text{Faradaic}}$ is the Faradaic efficiency of product k and η is the cell overpotential (or the sum of overpotentials on the cathode and anode). From this equation it becomes clear that high energy efficiency is achieved through a combination of high Faradaic efficiency for the desired product, and low overpotentials on the cathode and anode, because that will lead to a low cell potential. Note that at times researchers use a slightly different approach to determine the energy efficiency of their experimental setup [7[•]].

The Faradaic efficiency (sometimes also referred to as the current efficiency) for a given product is calculated using

$$\text{Eq. (2):} \quad \varepsilon_{\text{Faradaic}} = \frac{z \cdot n \cdot F}{Q} \quad (2)$$

where z is the number of electrons exchanged (e.g. $n = 2$ for reduction of CO₂ to CO), n the number of moles for a given product, F Faraday's constant ($F = 96\,485 \text{ C/mol}$), and Q the charge passed (C) [7[•],14[•],22].

The overall current density, defined as the current at a given cell potential divided by the active cathode electrode area (geometric surface area of the cathode), is a measure of the electrochemical reaction rate (conversion), so it helps determine the electrode area (and thus the electrolyzer size and capital investment) needed to meet the desired rate of producing the product. One can also calculate partial current densities for the individual products formed by multiplying overall current density by the corresponding FE.

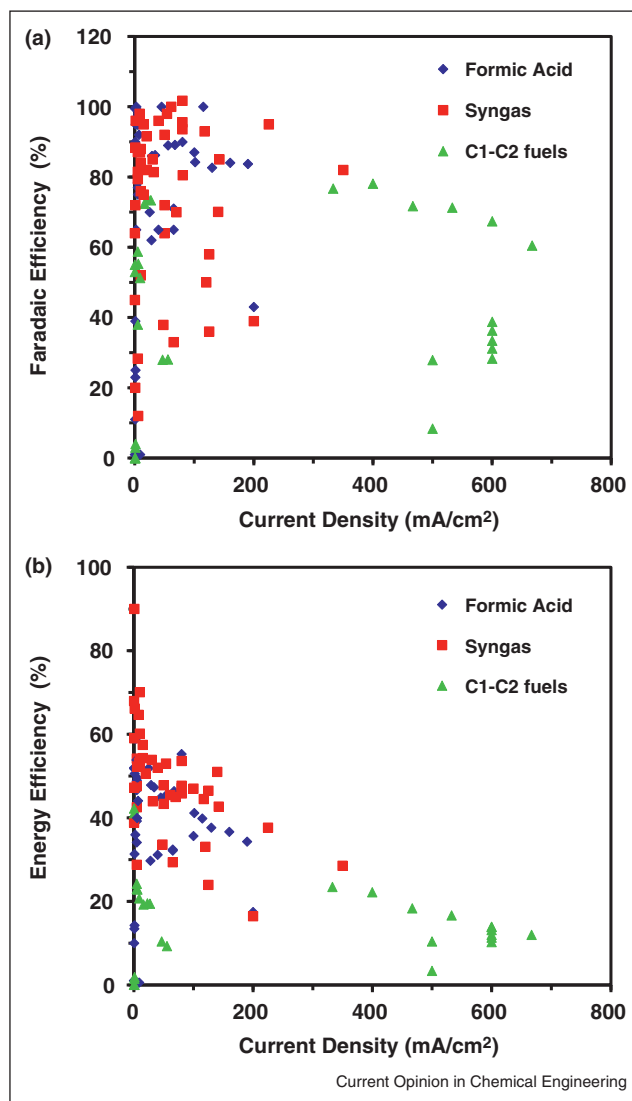
Current status and remaining challenges

Figure 1 shows plots of the energetic (Figure 1a) and Faradaic (Figure 1b) efficiencies versus current densities for CO₂ reduction to formic acid, syngas, and C1–C2 fuels (methane, ethylene and methanol) for data published in the literature from 1985 to December 2012. The data points that went into Figure 1 were chosen based on three criteria: the highest Faradaic efficiency, highest energetic efficiency, or highest current density achieved in a single report for the particular product. Note that many variables such as catalyst, electrode (plate, mesh, or gas diffusion electrode), electrolyte (composition and pH), cell configuration, temperature, and pressure are not consistent so this plot is only intended to provide a bigger picture of which figures of merit need most improvement. From these plots it is evident that for each of the different products, many examples have been reported exhibiting a high EE or a high FE, or a high CD, but that optimizing all three figures of merit has been a challenge. For example, for several cases of C1–C2 fuel production a high Faradaic efficiency in combination with a high current density has been achieved (as high as 70% FE with a CD of 600 mA/cm²; Figure 1a), but these same cases exhibit energetic efficiencies of less than 22%.

Catalysts

Electrocatalysts are needed to bind and activate CO₂ in order to reduce the high overpotentials typically encountered. Also, catalysts can drive selective formation of desired products. During the past few decades efforts have mostly focused on different metal catalysts and the various products that can be formed using those metals [4^{••},6,23,24]. Four distinct classes of metal catalysts have been identified for CO₂ reduction: (i) metals that mainly form formic acid, HCOOH (Pb, Hg, In, Sn, Cd, Tl); (ii) metals that mainly form carbon monoxide, CO (Au, Ag, Zn, Pd, Ga); (iii) metals that form significant amounts of

Figure 1



Summary of electrochemical performance for CO₂ conversion from selected literature in the period from 1985 to December 2012. (a) Faradaic efficiencies and (b) energetic efficiencies as a function of current density for three different (types of) products: formic acid [4^{••},14[•],28,29,31,32,51,57–63], syngas [4^{••},6,10,11,13^{••},26[•],27,30[•],35[•],38,53,54,61,63–71], and C1–C2 fuels (methane, ethylene, and methanol) [6,14[•],35[•],40,60,61,63,66,71].

hydrocarbons such as methane and ethylene (Cu); and (iv) metals that mainly form H₂ (Pt, Ni, Fe, Ti) [4^{••}]. Other potential products formed using metal catalysts include alcohols [17^{••}] and oxalic acid [25]. Over the last few years, researchers have also started to study other materials, including metal oxides [26[•],27,28], metal organic frameworks (MOFs) [29], as well as organometallic catalysts [30[•]]. In this review, we summarize work on heterogeneous catalysts that mainly form formic acid, CO, hydrocarbons, and methanol.

Formic acid

Formic acid can be produced with very high Faradaic efficiencies on metals with high overpotential for H₂ production, for example, Hg, Pb [4^{••}]. Metal oxides [28], alloys [31,32] and MOF catalysts [29] have also been found active for HCOOH production. Chen *et al.* found that a Sn/SnO_x catalyst exhibits much higher partial current density and Faradaic efficiency for HCOOH whereas Sn⁰ only produces H₂ [28]. This result suggests the participation of SnO_x in the CO₂ reduction pathway. Agarwal *et al.* showed that Sn-alloy catalysts yield higher Faradaic efficiencies than pure Sn at lower polarization [31]. Hinogami *et al.* synthesized a copper rubeanate metal organic framework (CR-MOF) catalyst which was able to decrease the onset for CO₂ reduction by 0.2 V compared to a plain Cu electrode [29].

Hydrocarbons

Copper catalysts seem uniquely capable of reducing CO₂ to hydrocarbons at ambient pressure and temperature [4^{••},14[•],20,33,34]. Recently, Jaramillo *et al.* have identified the many hydrocarbon products that form, and elucidated the mechanism by which these products form, using a flow cell with a Cu-based cathode [14[•]]. In a number of other studies, modifying copper surfaces has been shown to lower the overpotential and increase the selectivity for hydrocarbon formation. For example, Tang *et al.* found that a Cu electrode covered with Cu nanoparticles exhibits higher selectivity toward hydrocarbons due to a greater abundance of under-coordinated sites [35[•]]. Li *et al.* modified Cu electrodes by annealing Cu foil in air, which resulted in a stable electrode that lowered the overpotential for CO₂ reduction by 0.5 V compared to polycrystalline Cu [27]. Schouten *et al.* studied two single-crystal copper electrodes and observed two different mechanisms for ethylene formation [36].

Carbon monoxide

CO can also be produced with high Faradaic efficiency on various metal electrodes [4^{••}], and when combined with H₂ liquid fuels can be produced via the Fischer–Tropsch process. H₂ can be produced at less negative potential than CO, using fairly efficient processes (e.g. water electrolysis, biomass conversion, or the water gas shift reaction), so most efforts focus on optimizing the CO₂ conversion process with respect to maximizing CO production, although in some application scenarios a single reactor for cogenerating CO and H₂ may be preferred over two separate but more efficient reactors. Ag catalysts have long been the state of the art for CO production, with recently reported current densities as high as 91 mA/cm² [37^{••}], but other systems are also actively being studied. Rosen *et al.* reported being able to decrease the overpotential for CO production to 0.17 V, that is, they observed CO evolution at a cell potential of –1.5 V, close to the theoretical equilibrium cell potential of –1.33 V (difference between the equilibrium cathode

potential of -0.10 V and the equilibrium anode potential of 1.23 V), by using an aqueous ionic liquid solution, in which the 1-ethyl-3-methylimidazolium (EMIM⁺) cation serves as a co-catalyst, in combination with Ag nanoparticles immobilized on the electrode [13^{••}]. Unfortunately, the current densities reported in this work are low, less than 5 mA/cm². We have recently studied diaminotriazole-based organometallic silver catalysts, which decreased Ag loading by a factor of 20, while maintaining similar performance [30[•]]. Furthermore, a co-catalyst mechanism was also suggested by using those ligands. Interestingly, it is not clear whether the organometallic species is actually the catalytically active species on the electrode surface at this point. Salehi-Khojin *et al.* investigated the effect of Ag particle size on CO₂ reduction activity and observed maximum activity for particles with an average size of 5 nm Ag [38]. In another interesting lead, Chen *et al.* showed that Au nanoparticles synthesized by reduction of Au oxide films are highly selective for reduction of CO₂ to CO at overpotentials of about 0.14 V [26[•]].

Methanol

While methanol is a desirable product due to its wide range of application, including direct use as a fuel for a fuel cell, there are few reports on its formation from CO₂ via heterogeneous, electrochemical methods and these typically reported low current densities and/or low Faradaic efficiencies [39,40]. In contrast, homogeneous catalysis efforts for the conversion of CO₂ into methanol have been quite successful [41–43].

In summary, catalysts for the selective reduction of CO₂ into different interesting products have been developed, but catalysts that simultaneously exhibit overpotentials (e.g. <0.2 V) and current densities (e.g. >100 mA/cm²) needed for commercial applications are still lacking. The quest for such catalysts could be aided by more fundamental studies focusing on elucidation of reaction mechanisms for distinct catalysts, an area in which reports are few [36,44,45^{••}] and more in-depth modeling efforts, ideally linked directly with experimental work, so pathways for CO₂ reduction on different catalysts can be better understood, which in turn will assist the design and synthesis of novel catalysts that have both low overpotential and high activity for CO₂ reduction reactions.

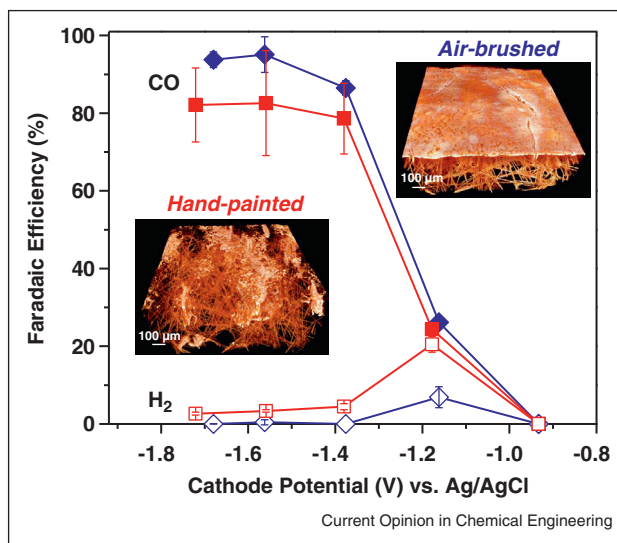
Electrode structure

Electrodes play a vital role in all devices based on heterogeneous electrochemical reactions, including those for CO₂ conversion. The performance and durability of the reactor are largely determined by the processes occurring at the electrode–electrolyte interface and within the electrode. In general, electrodes comprised a catalyst layer and a backing layer/substrate serve multiple functions: firstly to deliver reactant gas, CO₂, from flow-field channels to the catalyst layer, secondly to

transport product from the catalyst layer into flow channels or the electrolyte/membrane, and lastly to conduct electrons with low resistance [46,47]. Maximizing electrode performance, and consequently reactor performance, requires optimizing all of these transport processes that strongly depend on the complex structure of the electrode.

Despite their importance, to date only a few efforts have studied the interplay between electrode structure and performance [4^{••},7[•],12,37^{••},48]. In early work, Hori *et al.* extensively studied the CO₂ reduction reaction on planar metal electrodes (Cu, Au, Ag, Zn, Pd, Ga, Pb, Hg, In, Sn, Cd, Tl, Ni, Fe, Pt, Ti) at low current densities of about 5 mA/cm² [4^{••}]. Low surface area and low CO₂ concentrations at the electrode surface due to the limited CO₂ solubility in the aqueous electrolytes used limit the performance of such planar electrodes. Yano *et al.* proposed the use of a metal (Ag, Cu) mesh as the cathode for CO₂ reduction in a modified H-type cell in which the reaction can take place at a three-phase gas/solid/liquid interface by delivery of gaseous CO₂ from a gas chamber [12,48]. The lack of current density data in this report prevents quantification of the beneficial effects of this approach. More recently, Delacourt *et al.* hand-painted or spray-painted Ag catalyst inks on gas diffusion layers (GDLs) commonly used in polymer electrolyte membrane fuel cells, to generate cathodes with a Ag (particle size of 1 μm) loading of 8 – 10 mg/cm² [7[•]]. When this Ag nanoparticle-covered GDE (cathode) was mounted in a fuel cell-like CO₂ electrolysis cell with a buffer layer of 0.5 M KHCO₃ in contact with the Ag cathode, current densities as high as 20 mA/cm² were obtained, in combination with product selectivities for CO and H₂ that are comparable to the findings by Hori *et al.* [4^{••}] and Yano *et al.* [12] using similar catalysts (Ag) and electrolytes (0.5 M KHCO₃). We recently reported a current density as high as 91 mA/cm² in combination with 94% Faradaic efficiency for CO, and 46% energetic efficiency using a gas diffusion electrode (GDE) covered with a catalyst layer of Ag nanoparticles (particle size of 70 nm) [37^{••}]. The data were collected at room temperature and ambient pressure using a microfluidic CO₂ electrolysis cell in which a flowing aqueous KCl electrolyte separated the cathode (a GDE covered with a Ag catalyst layer) and anode (a GDE covered with a Pt catalyst layer). Deposition of the catalyst using a fully automated airbrushing method yielding a very thin (7 ± 2 μm measured using X-ray micro-computed tomography), crack free layer with a Ag loading of only 0.75 mg/cm² (Figure 2) was key to achieving this state-of-the-art performance, while simultaneously drastically reducing the amount of metal catalyst needed compared to planar metal electrodes, metal meshes, as well as other approaches to deposit metal nanoparticle-based inks. Furthermore, Salehi-Khojin *et al.* investigated how Ag particle size has a profound effect on CO₂ reduction activity [38]. They observed that

Figure 2



Example of the effect of catalyst layer deposition method (airbrushing vs. hand-painting) on electrode performance for converting CO₂ into CO [37^{**}]. Depositing Ag nanoparticle-based catalyst layers via fully automated air-brushing method led to a 3-fold increase in partial CO current density (not shown) and enhanced product selectivity (94% CO), despite a 10-fold decrease in catalyst loading compared to prior reports [37^{**}].

the reaction rate of the reduction of CO₂ to CO increases as the particle size decreases from 200 to 5 nm, but then drops again as the particle size decreases to 1 nm. Thus, a diameter of about 5 nm is likely an optimal particle size for Ag catalysts. In summary, use of a GDE in combination with optimized catalyst layer deposition methods has led to significant improvement in electrode performance for CO₂ reduction. Further efforts should probably focus on assessing, via experiment and modeling, to what extent the structure and chemical composition of the catalyst layer (e.g. pore size and distribution, the choice of binder materials such as Nafion) and the porous backing layer (e.g. porosity, hydrophobicity, layer thickness) impact the transport of reactants (sufficient supply of CO₂?) and products (active sites blocked?).

Electrolyte

Few efforts to date have focused on the effects of electrolyte composition on electrochemical CO₂ reduction, despite the fact that electrolytes have been known to affect almost every electrochemical process dating back to the days of Frumkin [49].

The heterogeneous electrochemical reduction of CO₂ employs aqueous electrolytes commonly comprised alkali cations (e.g. Na⁺, K⁺), various anions such as halide anions (e.g. Cl⁻), bicarbonate (HCO₃⁻), or hydroxide (OH⁻), and water [4^{**},33,50,51]. These inorganic salts are often used due to their high conductivities in water.

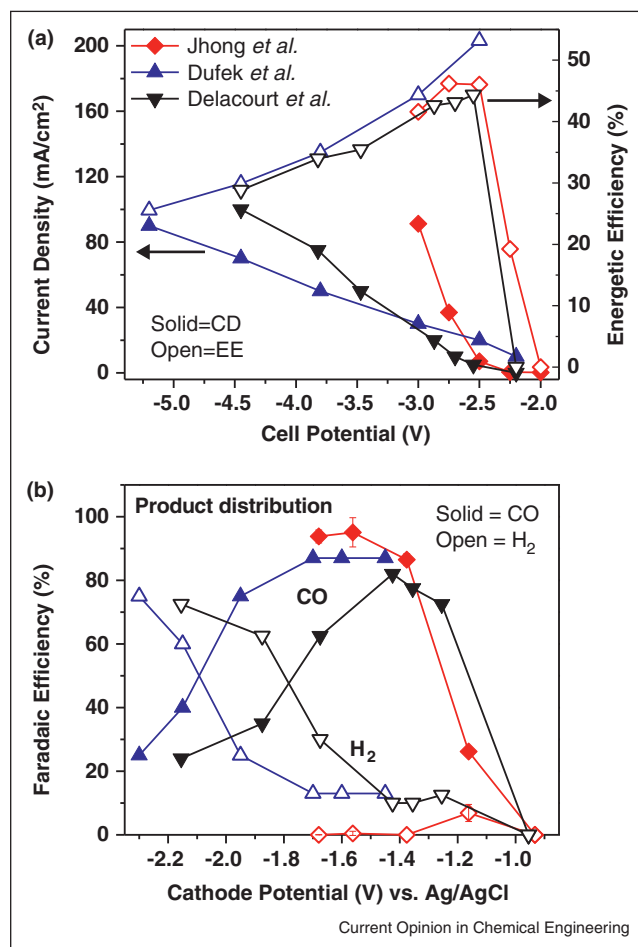
Additionally, the water in aqueous electrolytes provides protons for the necessary electrochemical proton transfer steps involved in the reaction pathway [4^{**},45^{**}]. A number of prior reports have shown that electrolyte choice has profound effects on current density, product selectivity, and energetic efficiency in CO₂ reduction [33,50,51]. For example, Hori *et al.* reported that cation choice (i.e. Li⁺, Na⁺, K⁺, and Cs⁺) for bicarbonate (HCO₃⁻) electrolytes significantly impacts the distribution of product formed on copper (Cu) electrodes [50]. Hori *et al.* also reported that anion choice (i.e. Cl⁻, ClO₄⁻, SO₄⁻, HCO₃⁻, H₂PO₄⁻), each with different buffer capacities, influences the local pH at the Cu electrode and thus the nature and the amount of products formed [33]. Similar to these findings by Hori *et al.*, Wu *et al.* observed significant differences in activity and selectivity of tin (Sn) electrodes when different electrolytes (KHCO₃, K₂SO₄, KCl, Na₂SO₄, Cs₂SO₄, NaHCO₃, and CsHCO₃) are used [51]. Previously, we reported that the size of the cation (Na⁺ < K⁺ < Rb⁺ < Cs⁺) of the salt used in the electrolyte plays a significant role in CO₂ reduction on silver (Ag) electrodes. Specifically, larger cations favor CO production and suppress H₂ evolution [52^{**}].

In summary, these studies show that (i) cation size impacts the propensity for cation adsorption on the electrode surface, which affects the potential of the outer Helmholtz plane (OHP) in the electrical double layer (EDL), and in turn impacts reaction energetics and kinetics; and (ii) the buffer capacity of anions impacts the local pH at the electrode and thus the availability of protons, which in turn affects reaction kinetics. Furthermore, depending on reactor configuration, electrolyte composition may enhance performance by improving the solubility of CO₂, for instance by using ionic liquids instead of aqueous solution, thereby reducing mass transport limitations.

Electrolyzers

No standard experimental setup or methodology for studying electrochemical CO₂ reduction currently exists. Different labs have used a variety of flow cells or electrolyzers for the various studies reported here. Jaramillo and coworkers [14^{*}], as well as our lab [5,30^{*},37^{**},52^{*}], use a microfluidic flow cell in which the electrodes are separated by a flowing liquid electrolyte, which enables analysis of individual electrode performance by using an external reference electrode. Delacourt *et al.* based their design on an alkaline fuel cell [7^{*}], while Dufek *et al.* used a more traditional electrolyzer design [10,11,53,54]. Interestingly, three of these systems exhibit similar behavior when comparing their performance for CO production (Figure 3). All data plotted in Figure 3 were collected at room temperature and ambient pressure to allow for fair comparison (identical kinetics) although these conditions might not be optimal for the reactors reported by Delacourt *et al.* and Dufek *et al.* Indeed,

Figure 3



Comparison of different electrolyzer configurations for electrochemical conversion of CO₂ to CO. Jhong *et al.*: a microfluidic flow cell [37^{••}]; Dufek *et al.*: a traditional electrolyzer [10]; and Delacourt *et al.*: a modified alkaline fuel cell [67]. The data from the literature plotted here were all collected at room temperature and ambient pressure.

Dufek *et al.* [10,54] have reported improved reactor performance at elevated temperature and/or pressure. The key difference between our recent data [37^{••}], and the data by the two other groups is that the same CDs and EEs can be achieved at much lower cell potentials. This difference can be completely attributed to the optimized structure of the catalyst layer in our flow cell-based electrolyzer. This suggests that electrolyzer design, which has a profound effect on mass transport, is presently not limiting the performance of CO₂ electrolyzers. Indeed, one would expect even better performance if these optimized catalyst layers would be used in reactors such as those reported by Delacourt *et al.* and Dufek *et al.* Still, further optimization of operating conditions (e.g. electrolyzers operated at elevated pressure and temperature) will continue to improve reactor performance in CO₂ reduction. Specifically, multiple labs have reported

enhanced current densities in pressurized electrolyzers (e.g. 20 atm) [32,55]. For example, Furuya *et al.* reported that a total current density as high as 300–900 mA/cm² can be achieved under 20 atm using a pressurized electrolyzer operated with GDEs coated with different metals (Pt, Ag, Cu, Ni, Co, Pd) [32].

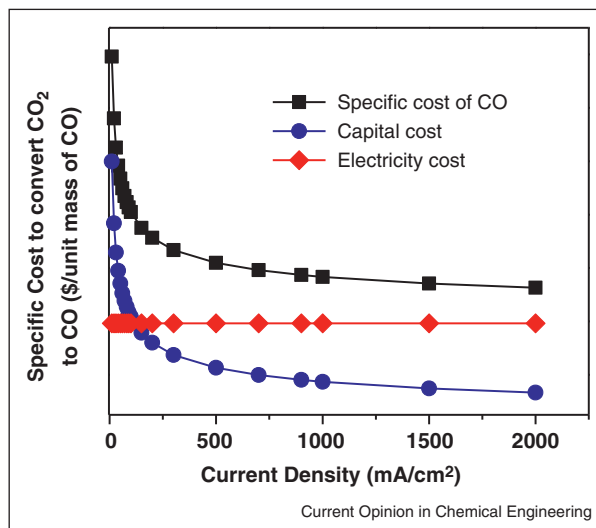
Future opportunities and concluding remarks

Recent reports on a variety of promising catalysts for CO₂ reduction (MOFs, organometallics, *etc.*) suggest that significant strides will be made to enhance catalyst activity while reducing overpotential. Such efforts will greatly benefit from fundamental mechanistic studies, as well as modeling of new classes of catalytic materials. Fine-tuning the electrolyte composition for a given catalyst offers a further opportunity for performance enhancement.

A key opportunity resides in optimization of electrode structure and/or composition. On the basis of our experience, CO₂ electrolysis is much more sensitive to the structure and composition of the microporous layer than similar electrodes in an identical cell operated as a fuel cell. Further efforts should probably focus on assessing, via experiment and modeling, to what extent the physical properties of these gas diffusion layers (e.g. porosity, hydrophobicity, layer thickness) impact effective gas-liquid phase separation while facilitating transport of reactants (sufficient supply of CO₂?) and products (active sites blocked?).

The above shows that multiple opportunities for further improvement of the EE, FE, and CD for electrochemical reduction of CO₂ to (intermediates for) value-added chemicals are available, but a few key questions remain: What combination of optimized figures of merit will be sufficient for economic feasibility? How fast do the component materials (particularly catalysts) degrade over long periods of time? What are the sources of CO₂ and how will potential contaminants such as sulfur-containing compounds impact electrolyzer design, as well as cell performance and catalyst durability [11]? Answering these questions requires a full system and life cycle analysis, well beyond the scope of this review. However we did start to develop a crude process cost analysis model [56] for the electrochemical reduction of CO₂ to CO to get an idea of how the cost to produce CO scales with current density (Figure 4). Many assumptions, including capital cost (e.g. non-linear correlation of capital cost and production rate) and the cost of electrical power (e.g. linear correlation of energy cost and production rate) went into this model, so on the *y*-axis we only show the specific cost to produce CO (\$/unit mass of CO produced) as well as the costs of capital investment and energy in arbitrary units. Critically, the cost to produce a given amount of CO is relatively high and dependent on the current density at which the electrolyzer is being operated below CD values of ~250 mA/cm², whereas the cost levels off if the process

Figure 4



Schematic representation of the results of a crude cost analysis model for the electrochemical conversion of CO₂ to CO: the relative cost of energy, capital investment, and the resulting CO cost as a function of the current density. The purpose of this graph is to visualize that the cost to produce CO is strongly dependent on current density below ~250 mA/cm², but levels off for higher current densities.

can be operated at higher current densities. One may conclude that the present state of the art performance of CDs around 100 mA/cm² (see e.g. [37]), is still far from a performance level where the cost to produce CO starts to level off. So indeed the performance of CO₂ electrolyzers needs to be improved significantly by development of better catalysts in combination with optimized electrode and electrolyte formulations. As mentioned above, estimation of the actual cost to produce CO (or other products) via electrochemical reduction of CO₂ will require the development of much more in depth cost and life cycle analysis models.

Acknowledgments

We gratefully acknowledge financial support from the Department of Energy (DE-FG02005ER46260), the Department of Energy through an STTR grant to Dioxide Materials and UIUC (DE-SC0004453), the National Science Foundation (CTS 05-47617), and the International Institute of Carbon Neutral Energy Research (WPI-I2CNER), sponsored by the World Premier International Research Center Initiative (WPI), MEXT, Japan. We also would like to thank the reviewers for their helpful input and Steven R Caliri for stimulating discussions.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest

1. Centi G, Perathoner S: **Opportunities and prospects in the chemical recycling of carbon dioxide to fuels.** *Catal Today* 2009, **148**:191-205.

2. Lackner KS: **Carbonate chemistry for sequestering fossil carbon.** *Annu Rev Energy Environ* 2002, **27**:193-232.
3. Whipple DT, Kenis PJA: **Prospects of CO₂ utilization via direct heterogeneous electrochemical reduction.** *J Phys Chem Lett* 2010, **1**:3451-3458.
4. Hori Y, Wakebe H, Tsukamoto T, Koga O: **Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal-electrodes in aqueous-media.** *Electrochim Acta* 1994, **39**:1833-1839.
5. Whipple DT, Finke EC, Kenis PJA: **Microfluidic reactor for the electrochemical reduction of carbon dioxide: the effect of pH.** *Electrochem Solid State Lett* 2010, **13**:D109-D111.
6. Hori Y, Kikuchi K, Suzuki S: **Production of CO and CH₄ in electrochemical reduction of CO₂ at metal-electrodes in aqueous hydrogencarbonate solution.** *Chem Lett* 1985:1695-1698.
7. Delacourt C, Ridgway PL, Kerr JB, Newman J: **Design of an electrochemical cell making syngas (CO + H₂) from CO₂ and H₂O reduction at room temperature.** *J Electrochem Soc* 2008, **155**:B42-B49.

Seminal paper that tabulates the activity of many metals towards CO₂ reduction into a range of products.

8. Delacourt C, Ridgway PL, Newman J: **Mathematical modeling of CO₂ reduction to CO in aqueous electrolytes I. Kinetic study on planar silver and gold electrodes.** *J Electrochem Soc* 2010, **157**:B1902-B1910.
9. Delacourt C, Newman J: **Mathematical modeling of CO₂ reduction to CO in aqueous electrolytes II. Study of an electrolysis cell making syngas (CO + H₂) from CO₂ and H₂O reduction at room temperature.** *J Electrochem Soc* 2010, **157**:B1911-B1926.
10. Dufek EJ, Lister TE, McIlwain ME: **Bench-scale electrochemical system for generation of CO and syn-gas.** *J Appl Electrochem* 2011, **41**:623-631.
11. Dufek EJ, Lister TE, McIlwain ME: **Influence of S contamination on CO₂ reduction at Ag electrodes.** *J Electrochem Soc* 2011, **158**:B1384-B1390.
12. Yano H, Shirai F, Nakayama M, Ogura K: **Electrochemical reduction of CO₂ at three-phase (gas vertical bar liquid vertical bar solid) and two-phase (liquid vertical bar solid) interfaces on Ag electrodes.** *J Electroanal Chem* 2002, **533**:113-118.
13. Rosen BA, Salehi-Khojin A, Thorson MR, Zhu W, Whipple DT, Kenis PJA, Masel RI: **Ionic liquid-mediated selective conversion of CO₂ to CO at low overpotentials.** *Science* 2011, **334**:643-644.

This work demonstrates the use of aqueous ionic liquid solutions for electrochemical CO₂ reduction to CO, in which the cation of the ionic liquid acts as a cocatalyst.

14. Kuhl KP, Cave ER, Abram DN, Jaramillo TF: **New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces.** *Energy Environ Sci* 2012, **5**:7050-7059.
 15. Savéant J-M: **Molecular catalysis of electrochemical reactions. Mechanistic aspects.** *Chem Rev* 2008, **108**:2348-2378.
 16. Benson EE, Kubiak CP, Sathrum AJ, Smieja JM: **Electrocatalytic and homogeneous approaches to conversion of CO₂ to liquid fuels.** *Chem Soc Rev* 2009, **38**:89-99.
 17. Hori Y: **CO₂-reduction, catalyzed by metal electrodes.** •• *Handbook of Fuel Cells.* John Wiley & Sons, Ltd.; 2010.
- This book chapter provides an excellent overview of the general ideas behind electrochemical reduction of CO₂ on metal electrodes, including catalyst and electrolyte selection, and reaction mechanisms.

18. Dörner RW, Hardy DR, Williams FW, Willauer HD: **Heterogeneous catalytic CO₂ conversion to value-added hydrocarbons.** *Energy Environ Sci* 2010, **3**:884-890.
19. Kumar B, Llorente M, Froehlich J, Dang T, Sathrum A, Kubiak CP: **Photochemical and photoelectrochemical reduction of CO₂.** *Annu Rev Phys Chem* 2012, **63**:541.
20. Gattrell M, Gupta N, Co A: **A review of the aqueous electrochemical reduction of CO₂ to hydrocarbons at copper.** *J Electroanal Chem* 2006, **594**:1-19.
21. Oloman C, Li H: **Electrochemical processing of carbon dioxide.** *Chemsuschem* 2008, **1**:385-391.
 This study reports the multi-cell trickle-bed electrochemical reactors for the reduction of CO₂ into formate under industrial conditions. Material balance and economic viability of the process are analyzed in this study.
22. Wu J, Risalvato F, Zhou X-D: **Effects of the electrolyte on electrochemical reduction of CO₂ on Sn electrode.** *ECS Trans* 2012, **41**:49-60.
23. Azuma M, Hashimoto K, Hiramoto M, Watanabe M, Sakata T: **Electrochemical reduction of carbon-dioxide on various metal-electrodes in low-temperature aqueous KHCO₃ media.** *J Electrochem Soc* 1990, **137**:1772-1778.
24. Ikeda S, Takagi T, Ito K: **Selective formation of formic-acid. Oxalic-acid and carbon-monoxide by electrochemical reduction of carbon-dioxide.** *Bull Chem Soc Jpn* 1987, **60**:2517-2522.
25. Tomita Y, Teruya S, Koga O, Hori Y: **Electrochemical reduction of carbon dioxide at a platinum electrode in acetonitrile-water mixtures.** *J Electrochem Soc* 2000, **147**:4164-4167.
26. Chen Y, Li CW, Kanan MW: **Aqueous CO₂ reduction at very low overpotential on oxide-derived Au nanoparticles.** *J Am Chem Soc* 2012, **134**:19969-19972.
 This work reports that Au catalyst exhibits high selectivity for CO₂ reduction to CO in aqueous solution at only 140 mV overpotential.
27. Li CW, Kanan MW: **CO₂ reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu₂O films.** *J Am Chem Soc* 2012, **134**:7231-7234.
28. Chen YH, Kanan MW: **Tin oxide dependence of the CO₂ reduction efficiency on tin electrodes and enhanced activity for tin/tin oxide thin-film catalysts.** *J Am Chem Soc* 2012, **134**:1986-1989.
29. Hinogami R, Yotsuhashi S, Deguchi M, Zenitani Y, Hashiba H, Yamada Y: **Electrochemical reduction of carbon dioxide using a copper rubeanate metal organic framework.** *ECS Electrochem Lett* 2012, **1**:H17-H19.
30. Tornow CE, Thorson MR, Ma S, Gewirth AA, Kenis PJA: **Nitrogen-based catalysts for the electrochemical reduction of CO₂ to CO.** *J Am Chem Soc* 2012, **134**:19520-19523.
 This work reports organometallic Ag catalysts with very high mass activity for electrochemical reduction of CO₂ to CO. A cocatalyst mechanism involving nitrogen species is suggested.
31. Agarwal AS, Zhai YM, Hill D, Sridhar N: **The electrochemical reduction of carbon dioxide to formate/formic acid: engineering and economic feasibility.** *Chemsuschem* 2011, **4**:1301-1310.
32. Furuya N, Yamazaki T, Shibata M: **High performance Ru-Pd catalysts for CO₂ reduction at gas-diffusion electrodes.** *J Electroanal Chem* 1997, **431**:39-41.
33. Hori Y, Murata A, Takahashi R: **Formation of hydrocarbons in the electrochemical reduction of carbon-dioxide at a copper electrode in aqueous-solution.** *J Chem Soc Faraday Trans I* 1989, **85**:2309-2326.
34. Cook RL, Macduff RC, Sammells AF: **High-rate gas-phase CO₂ reduction to ethylene and methane using gas-diffusion electrodes.** *J Electrochem Soc* 1990, **137**:607-608.
35. Tang W, Peterson AA, Varela AS, Jovanov ZP, Bech L, Durand WJ, Dahl S, Norskov JK, Chorkendorff I: **The importance of surface morphology in controlling the selectivity of polycrystalline copper for CO₂ electroreduction.** *Phys Chem Chem Phys* 2012, **14**:76-81.
 This modeling study (DFT calculations) predicts that roughened copper surfaces have higher selectivities towards hydrocarbon products due to the increased abundance of undercoordinated sites, which according to the outcomes of the DFT calculations are active sites.
36. Schouten KJP, Qin Z, Gallent EP, Koper MTM: **Two pathways for the formation of ethylene in CO reduction on single-crystal copper electrodes.** *J Am Chem Soc* 2012, **134**:9864-9867.
37. Jhong HR, Brushett FR, Kenis PJA: **The effects of catalyst layer deposition methodology on electrode performance.** *Adv Energy Mater* available early view (online version of record published before inclusion in an issue)
 This study reports on the importance of depositing thin and crack free catalyst layers, which resulted in the state-of-the-art combination of EE, FE and current density at the time of submission of this review.
38. Salehi-Khojin A, Jhong H-RM, Rosen BA, Zhu W, Ma S, Kenis PJA, Masel RI: **Nanoparticle silver catalysts that show enhanced activity for carbon dioxide electrolysis.** *J Phys Chem C* 2012, **117**:1627-1632.
39. Arai G, Harashina T, Yasumori I: **Selective electrocatalytic reduction of carbon dioxide to methanol on Ru-modified electrode.** *Chem Lett* 1989, **18**:1215-1218.
40. Le M, Ren M, Zhang Z, Sprunger PT, Kurtz RL, Flake JC: **Electrochemical reduction of CO₂ to CH₃OH at copper oxide surfaces.** *J Electrochem Soc* 2011, **158**:E45-E49.
41. Seshadri G, Lin C, Bocarsly AB: **A new homogeneous electrocatalyst for the reduction of carbon dioxide to methanol at low overpotential.** *J Electroanal Chem* 1994, **372**:145-150.
42. Barton Cole E, Lakkaraju PS, Rampulla DM, Morris AJ, Abelev E, Bocarsly AB: **Using a one-electron shuttle for the multielectron reduction of CO₂ to methanol: kinetic, mechanistic, and structural insights.** *J Am Chem Soc* 2010, **132**:11539-11551.
43. Barton EE, Rampulla DM, Bocarsly AB: **Selective solar-driven reduction of CO₂ to methanol using a catalyzed p-GaP based photoelectrochemical cell.** *J Am Chem Soc* 2008, **130**:6342-6344.
44. Chandrasekaran K, Bockris LOM: **In-situ spectroscopic investigation of adsorbed intermediate radicals in electrochemical reactions: CO₂⁻ on platinum.** *Surf Sci* 1987, **185**:495-514.
45. Peterson AA, Abild-Pedersen F, Studt F, Rossmeisl J, Norskov JK: **How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels.** *Energy Environ Sci* 2010, **3**:1311-1315.
 This computational study focuses on understanding the rate limiting steps in the formation of hydrocarbons from CO₂, and reveals that the binding energy of CO on metal surfaces is a key determinant of the overpotential for CO₂ reduction.
46. Cindrella L, Kannan AM, Lin JF, Saminathan K, Ho Y, Lin CW, Wertz J: **Gas diffusion layer for proton exchange membrane fuel cells – a review.** *J Power Sources* 2009, **194**:146-160.
47. Jhong HR, Brushett FR, Yin LL, Stevenson DM, Kenis PJA: **Combining structural and electrochemical analysis of electrodes using micro-computed tomography and a microfluidic fuel cell.** *J Electrochem Soc* 2012, **159**:B292-B298.
48. Yano H, Shirai F, Nakayama M, Ogura K: **Efficient electrochemical conversion of CO₂ to CO, C₂H₄ and CH₄ at a three-phase interface on a Cu net electrode in acidic solution.** *J Electroanal Chem* 2002, **519**:93-100.
49. Frumkin AN: **Influence of cation adsorption on the kinetics of electrode processes.** *Trans Faraday Soc* 1959, **55**:156-167.
50. Murata A, Hori Y: **Product selectivity affected by cationic species in electrochemical reduction of CO₂ and CO at a Cu electrode.** *Bull Chem Soc Jpn* 1991, **64**:123-127.
51. Wu JJ, Risalvato FG, Ke FS, Pellechia PJ, Zhou XD: **Electrochemical reduction of carbon dioxide I. Effects of the electrolyte on the selectivity and activity with Sn electrode.** *J Electrochem Soc* 2012, **159**:F353-F359.
52. Thorson MR, Siil SI, Kenis PJA: **Effect of cations on the electrochemical conversion of CO₂ to CO.** *J Electrochem Soc* 2013, **160**:F69-F74.

This study highlights the importance of electrolyte composition by comparing the performance of a CO₂ electrolyzer in the presence of different salt solutions.

53. Dufek EJ, Lister TE, McIlwain ME: **Influence of electrolytes and membranes on cell operation for syn-gas production.** *Electrochem Solid State Lett* 2012, **15**:B48-B50.
54. Dufek EJ, Lister TE, Stone SG, McIlwain ME: **Operation of a pressurized system for continuous reduction of CO₂.** *J Electrochem Soc* 2012, **159**:F514-F517.
55. Sonoyama N, Kirii M, Sakata T: **Electrochemical reduction of CO₂ at metal-porphyrin supported gas diffusion electrodes under high pressure CO₂.** *Electrochem Commun* 1999, **1**:213-216.
56. Prince-Richard S, Whale M, Djilali N: **A techno-economic analysis of decentralized electrolytic hydrogen production for fuel cell vehicles.** *Int J Hydrogen Energy* 2005, **30**:1159-1179.
57. Whipple DT, Jayashree RS, Egas D, Alonso-Vante N, Kenis PJA: **Ruthenium cluster-like chalcogenide as a methanol tolerant cathode catalyst in air-breathing laminar flow fuel cells.** *Electrochim Acta* 2009, **54**:4384-4388.
58. Innocent B, Liaigre D, Pasquier D, Ropital F, Léger JM, Kokoh KB: **Electro-reduction of carbon dioxide to formate on lead electrode in aqueous medium.** *J Appl Electrochem* 2009, **39**:227-232.
59. Köleli F, Atilan T, Palamut N, Gizir AM, Aydin R, Hamann CH: **Electrochemical reduction of CO₂ at Pb- and Sn-electrodes in a fixed-bed reactor in aqueous K₂CO₃ and KHCO₃ media.** *J Appl Electrochem* 2003, **33**:447-450.
60. Kaneco S, Iwao R, Iiba K, Ohta K, Mizuno T: **Electrochemical conversion of carbon dioxide to formic acid on Pb in KOH/methanol electrolyte at ambient temperature and pressure.** *Energy* 1998, **23**:1107-1112.
61. Saeki T, Hashimoto K, Fujishima A, Kimura N, Omata K: **Electrochemical reduction of CO₂ with high current density in a CO₂-methanol medium.** *J Phys Chem* 1995, **99**:8440-8446.
62. Mahmood MN, Mashed D, Harty CJ: **Use of gas-diffusion electrodes for high-rate electrochemical reduction of carbon dioxide. II. Reduction at metal phthalocyanine-impregnated electrodes.** *J Appl Electrochem* 1987, **17**:1223-1227.
63. Furuya N, Koide S: **Electroreduction of carbon dioxide by metal phthalocyanines.** *Electrochim Acta* 1991, **36**:1309-1313.
64. Rosen BA, Salehi-Khojin A, Thorson MR, Zhu W, Whipple DT, Kenis PJA, Masel RI: **Ionic liquid-mediated selective conversion of CO₂ to CO at low overpotentials.** *Science* 2011, **334**:643-644.
65. Yamamoto T, Tryk DA, Fujishima A, Ohata H: **Production of syngas plus oxygen from CO₂ in a gas-diffusion electrode-based electrolytic cell.** *Electrochim Acta* 2002, **47**:3327-3334.
66. Frese KW, Leach S: **Electrochemical reduction of carbon-dioxide to methane, methanol, and CO on Ru electrodes.** *J Electrochem Soc* 1985, **132**:259-260.
67. Delacourt C, Ridgway PL, Kerr JB, Newman J: **Design of an electrochemical cell making syngas (CO + H₂) from CO₂ and H₂O reduction at room temperature.** *J Electrochem Soc* 2008, **155**:B42-B49.
68. Xie K, Zhang YQ, Meng GY, Irvine JTS: **Electrochemical reduction of CO₂ in a proton conducting solid oxide electrolyser.** *J Mater Chem* 2011, **21**:195-198.
69. Li YX, Zhou JE, Dong DH, Wang Y, Jiang JZ, Xiang HF, Xie K: **Composite fuel electrode La_{0.2}Sr_{0.8}TiO₃-delta-Ce_{0.8}Sm_{0.2}O₂-delta for electrolysis of CO₂ in an oxygen-ion conducting solid oxide electrolyser.** *Phys Chem Chem Phys* 2012, **14**:15547-15553.
70. Aeshala LM, Rahman SU, Verma A: **Effect of solid polymer electrolyte on electrochemical reduction of CO₂.** *Sep Purif Technol* 2012, **94**:131-137.
71. Hara K, Sakata T: **Electrocatalytic formation of CH₄ from CO₂ on a Pt gas diffusion electrode.** *J Electrochem Soc* 1997, **144**:539-545.