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Chapter

Heterogeneous Electrocatalysts for CO_2 Reduction to Value Added Products
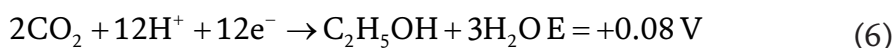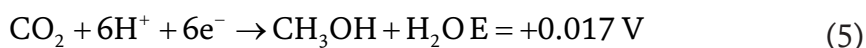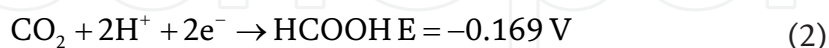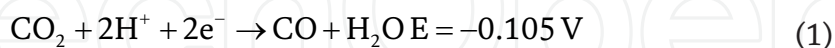
M. Amin Farkhondehfal and Juqin Zeng

Abstract

The CO_2 that comes from the use of fossil fuels accounts for about 65% of the global greenhouse gas emission, and it plays a critical role in global climate changes. Among the different strategies that have been considered to address the storage and reutilization of CO_2, the transformation of CO_2 into chemicals and fuels with a high added-value has been considered a winning approach. This transformation is able to reduce the carbon emission and induce a "fuel switching" that exploits renewable energy sources. The aim of this chapter is to categorize different heterogeneous electrocatalysts which are being used for CO_2 reduction, based on the desired products of the above mentioned reactions: from formic acid and carbon monoxide to methanol and ethanol and other possible by products. Moreover, a brief description of the kinetic and mechanism of the CO_2 reduction reaction) and pathways toward different products have been discussed.

Keywords: CO_2 electroreduction, electrocatalyst, faradaic efficiency, metal-based

1. Introduction

Nowadays, global warming and CO_2 emissions as well as atmospheric CO_2 concentration are central topics in politics and scientific debate. The global energy supply based on fossil fuels has reached an unprecedented scale leading to excess anthropogenic CO_2 emission. CO_2 accumulates in the atmosphere and its concentration has surpassed 409 ppm in 2019 much higher than the 270 ppm during the pre-industrial era [1]. As a well-known greenhouse gas, accumulated CO_2 traps more infrared radiation, breaking the energy balance on the earth's surface. Using CO_2 as feedstock to produce valuable carbon-based chemicals is considered to be a feasible approach to close the carbon cycle and mitigate the climate change. Many strategies have been developed for CO_2 valorisation, including thermochemical, photochemical, electrochemical and biological approaches [2–5]. Among these methods, electrochemical conversion presents several advantages. Firstly, this method can use green chemicals as electrolytes and electricity from renewable energy sources, thus not contributing to new CO_2 emissions while transforming it [6]. Secondly, the products and conversion rates can be tuned by utilizing different catalysts and applying various potentials [7, 8]. Finally, the electrolyzer and electrolysis process for CO_2 conversion can be developed based on the already existing technologies

such as water electrolyzers, polymer electrolyte membrane fuel cells, solid oxide fuel cells and so on [9]. However, the CO_2 reduction reaction (CO_2RR) involves several proton-assisted multiple-electron-transfer processes with similar standard potentials (V *vs* the reversible hydrogen electrode (RHE), Reactions (1)-(6) [10], leading to the formation of carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), ethylene (C_2H_4), methanol (CH_3OH) and ethanol (C_2H_5OH). Moreover, hydrogen (H_2) evolution is the competing reaction in aqueous solution (Reaction (7)). Therefore, it is a challenge to control the selectivity of the CO_2RR from the thermodynamic view.

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \ E = -0.105 \, V \tag{1}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \ E = -0.169 \, V \tag{2}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \ E = +0.169 \, V \tag{3}$$

$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O \ E = +0.079 \, V \tag{4}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \ E = +0.017 \, V \tag{5}$$

$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O \ E = +0.08 \, V \tag{6}$$

$$2H^+ + 2e^- \rightarrow H_2 \ E = 0.000 \, V \tag{7}$$

From the kinetic point of view, it is even more challenging to form chemical bonds for the complex and energetic molecule products [11]. Transferring one electron to the adsorbed CO_2 molecule to activate it (generating the radical CO_2^{*-}) is believed to be the rate-determining step of the CO_2RR on transition metal-based catalysts because of the high activation barrier needed for this step [12]. Consequently, much more negative potentials than the standard ones are needed to drive the CO_2RR. Therefore, an appropriately designed catalyst is essential in order to activate the CO_2 molecules. Once CO_2^{*-} forms on the catalyst's surface, its reactivity in this state controls the distribution of final products. Both early and later studies [13–15] of electrochemical CO_2RR on various metal-based electrodes found that the radical CO_2^{*-} interacts with the surface of the catalyst in different ways, depending on the intrinsic electronic surface's properties of the material. Hence, a suitable catalyst is necessary in order to selectively drive the CO_2RR and to obtain a specific product. In the present chapter, numerous electrocatalysts are classified based on the CO_2RR product, involving the reaction pathways and mechanism study.

2. CO-selective catalysts

CO is an important product from the reduction of CO_2 since it has high relevance for the chemical industry [16]. It is considered the most important C_1-building block and is intensively used in large industrial processes such as Fischer-Tropsch synthesis of hydrocarbons and Monsanto/Cativa acetic acid synthesis. By a techno-economic analysis that takes into consideration the costs of CO_2, electricity, separation, capital and maintenance, operation and the known product selectivity

and outputs the levelized cost of the chemical produced, CO is one of the most economically viable and atom-economic targets [17].

In recent years, great efforts have been dedicated to the study of electrocatalysts for the electrochemical CO₂RR to CO. **Table 1** summarizes the most widely investigated types.

Electrocatalyst	Electrolyte	Potential (V vs. RHE)	Faradaic efficiency (%)	Current density (−mA cm⁻²)	Reference
Au Nanoparticles	0.5 M KHCO₃	−0.67	90	5	[18]
Au needles	0.5 M KHCO₃	−0.35	95	15	[19]
Ag nanowires	0.5 M KHCO₃	−0.6	90	4.9	[20]
Nanoporous Ag	0.5 M KHCO₃	−0.6	92	18	[21]
Ag-TiO₂	0.1 M KHCO₃	−1.3	35	30	[20]
Zn nanoparticles	0.1 M KHCO₃	−0.95	98.1	17.5	[22]
ZnO particles	0.1 M KHCO₃	−0.89	68	3.0	[8]
Cu-Sn foam	0.1 M KHCO₃	−0.8	93	6.7	[23]
Cu-Sn	0.1 M KHCO₃	−0.6	90	1.0	[24]
Cu-SnO₂	0.5 M KHCO₃	−0.7	93	4.6	[25]
Zn₉₄Cu₆ foam	0.5 M KHCO₃	−0.95	90	8.0	[26]
CuO-Sb₂O₃	0.1 M KHCO₃	−0.8	90	5.0	[27]
SnOₓ/Ag	0.5 M KHCO₃	−0.6	85	0.7	[28]
AuCu	0.1 M KHCO₃	−0.8	50	—	[29]
Mn-N-C	0.1 M KHCO₃	−0.6	~80	< 5	[30]
Fe-N-C					
MnFe-N-C					
Ni-N-C	0.1 M KHCO₃	−1.0	95	15	[31]
Ni-N-C	0.1 M KHCO₃	−0.81	80	13	[32]
FeN₄/C	0.1 M KHCO₃	−0.6	93	1.5	[33]
FeN₅/Graphene	0.1 M KHCO₃	−0.46	97	1.8	[34]
Fe³⁺–N–C	0.5 M KHCO₃	−0.47	95	21	[35]
Zn-N-Graphene	0.5 M KHCO₃	−0.5	91	10	[36]
ZnN₄/C	0.5 M KHCO₃	−0.43	95	4.8	[37]
Sb-NC	0.1 M KHCO₃	−0.9	82	2.9	[38]
Ni/Fe-N-C	0.5 M KHCO₃	−0.7	98	7.4	[39]
COF₃₆₆-Co	0.5 M KHCO₃	−0.67	87	—	[40]
COF₃₆₆-Co, COF₃₆₇-Co	0.5 M KHCO₃	−0.66	91	3.3	[41]
Fe porphyrin-graphene hydrogel	0.1 M KHCO₃	−0.39	96	0.42	[42]
Fe(III) porphyrin/ graphene	0.1 M KHCO₃	−0.54	98.7	1.68	[43]

Table 1.
CO-selective catalysts for the CO2RR.

2.1 Metals and bimetallic materials

From both experimental and theoretical studies, Au, Ag and Zn are the most selective metals for CO formation. The CO_2RR on Au and Ag is characterized by low overpotentials, excellent selectivity and high activity [18–20, 30, 44]. On contrast, Zn shows relatively higher overpotentials, lower activity and moderate-to-high selectivity [8, 21].

Many bimetallic materials are demonstrated to selectively catalyze the CO_2RR to CO, including Cu-Sn [22–24], Cu-Zn [25], Cu-Sb [26], Cu-Ag [27], Cu-Au [28] and so on. Among all these materials, Cu-Sn catalysts have attracted the most intensive attention due to the high selectivity, good activity and outstanding repeatability. In addition, compared with others, Cu and Sn are relatively more abundant and more cost-effective, making Cu-Sn catalysts more suitable for the large-scale implementation. Hence, further study on the Cu-Sn catalysts is expected to bring benefits to both the academic and industrial sectors related to the CO_2 valorization.

2.2 Single metal atom supported on N-doped carbon

Single-metal-atom catalysts supported on porous N-doped carbon represent a class of catalysts with high atom efficiency. After introduced in 2015 by Varela et al. [30], it has gained much attention for CO_2 reduction. Ni supported on N-C, in contrast to Ni nanoparticles that are known to be effective in the HER, is reported to be an efficient electrocatalyst for the CO_2RR to CO [29, 31, 32]. Various types of Fe-N active sites have been identified and demonstrated to selectively promote the CO formation at very low overpotentials [29, 33–35]. Compared to the metallic Zn and ZnO, single atom Zn sites show much lower overpotentials where excellent CO selectivity has obtained [36, 37]. Sb atomic sites, compared to bulk Sb, Sb_2O_3, and Sb nanoparticles that exhibit poor activity and selectivity for the CO_2RR, enable the CO formation with good selectivity at relatively high overpotentials [38]. Isolated diatomic Ni-Fe sites anchored on nitrogenated carbon are also studied as an electrocatalyst for CO_2 reduction [39]. The catalyst exhibits high selectivity with CO Faradaic efficiency above 90% over a wide potential range from −0.5 to −0.9 V (98% at −0.7 V, vs. RHE), and robust durability.

Single atoms of selected transition metals anchored in N-doped carbon have emerged as unique and promising electrocatalysts because of the maximal atom utilization and high efficiency. Most of them perform differently from their bulk metal or oxide species, due to the metal–matrix interfacial interaction that leads to the manipulation of the electronic structures of the materials and to the emergence of additional active sites. Despite the big progress made in the recent years, many challenges remain in the development of the single atom catalysts. For example, the loading of metals is usually low, leading to relatively low geometric current density and thus limitations for practical applications. In addition, big efforts have to focus on **both** the synthetic front and structural characterizations and these necessitate the development of effective computational methods and characterization tools.

2.3 Immobilized molecular catalysts

Homogeneous electrocatalysis constitutes an efficient way of converting CO_2 to various products but some distinct challenges persist [44]. For example, the catalyst stability and recyclability are usually poor; only a small portion of the catalyst molecules at the reaction interface is active, while most of them are passive; some catalysts have poor solubility; product separation could be difficult. To overcome these disadvantages, great efforts have been dedicated to the immobilization of
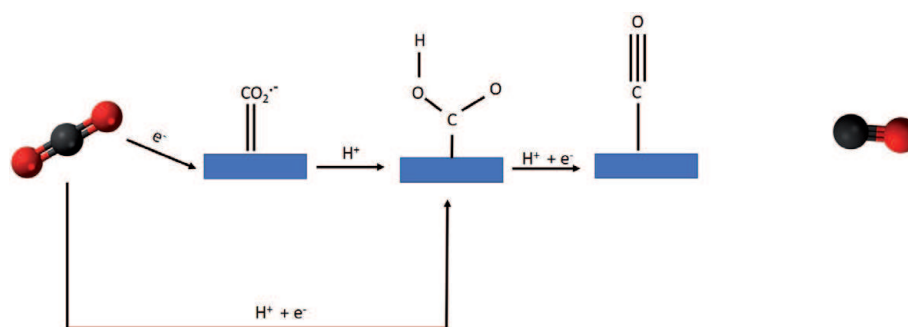
Figure 1.
Schematic of possible pathways for CO production.

molecular catalysts on electrode surfaces for the heterogeneous CO_2RR. Being fixed on carbon supports, the porphyrin- and phthalocyanine-based catalysts with Fe and Co centers are very selective for CO formation at relatively low overpotentials [41–43, 45]. The catalytic performance can be affected by both the intrinsic properties of the catalysts such as the structure and the metal center, and the extrinsic factors such as the catalyst immobilization methods, the support material and the catalyst loading. A deeper understanding of those intrinsic and extrinsic factors can enable the optimization of supported molecular catalysts in order to achieve the CO_2RR performance as high as that of the nanostructured metals, metal alloys and single atom catalysts supported on N-carbon materials [16].

The mechanism study of CO_2RR on metal-based materials is widely studied, in combination of in-situ spectroscopic analyses and DFT calculations [45, 46]. As shown in **Figure 1**, it is suggested that the CO_2RR to CO process on metallic Zn or Ag surface includes four elementary reaction steps: (1) one electron transfers to CO_2 to form CO_2^{*-}; (2) one proton transfers to CO_2^{*-} to obtain $COOH^*$ intermediate; (3) an electron and a proton transfer to $COOH^*$ to form CO^*; (4) CO^* desorbs to produce CO. Another possible pathway is supposed to include three main steps: (1) an electron coupled with a proton transfers to CO_2 to form $COOH^*$ intermediate; (2) another electron coupled with a proton transfers to $COOH^*$ to form CO^*; (3) CO^* desorbs to produce CO.

3. Formate-selective catalysts

Due to the large storage and safety requirements for CO during carbon sequestration and storage (CCS), the production of liquid formic acid is becoming a more attractive solution. Formic acid could be directly used as a feedstock for fuel cells and as a precursor for manufacturing value-added chemicals such as formate esters, methanol, and other carboxylic acids and derivatives [47]. Some heavy metals, including Pb, Hg, In, Cd, and Tl, are efficient electrocatalysts for converting CO_2 into formate/formic acid. However, the defects of the high toxicity and/or high cost are standing in the way for their large-scale applications [48]. Other earth abundant metals like Sn, Cu and Bi gained a lot of attentions in recent years. **Table 2** has summarized some of the important results for formic acid production through electrocatalysis of CO_2.

3.1 Metal and metal oxides

From the pioneer work of *Hori* eta al. [57], the metals Pb, Hg, In, Sn, Cd and Tl are selective for HCOOH formation. Among them, Sn and SnO_x catalysts have become the most interesting one due to the high selectivity and their non-noble, eco-friendly

Electrocatalyst	Electrolyte	Potential (V vs. RHE)	Current Density ($-mA\ cm^{-2}$)	FE (%)	Reference
B-doped Pd	0.1 M KHCO$_3$	−0.5 V	10	70	[49]
S-modified Cu	0.1 M KHCO$_3$	−0.8	20	80	[50]
Pd needles	0.5 M KHCO$_3$	−0.2	10	91	[19]
Sn(S)/Au	0.1 M KHCO$_3$	−0.75	55	94	[51]
nano-SnO$_2$/C	0.1 M NaHCO$_3$	−1.16	6.2	86.2	[52]
BiOx/C	0.5 M NaCl	−1.13	12.5	96	[53]
Cu–Au	0.5 M KHCO$_3$	−0.6	10.2	81	[54]
Bi nanotubes	0.5 M KHCO$_3$	−1	39.4	97	[48]
Sulfur-doped indium	0.5 M KHCO$_3$	−0.98	58.9	95	[55]
SnO$_2$	0.1 M KHCO$_3$	−1.06	11	82	[56]

Table 2.
Formate-selective catalysts for the CO2RR.

and low-cost characteristics [56]. Recently, Pd demonstrates to be an appealing catalyst for HCOOH formation, showing high activity and good stability at extremely low overpotentials [19, 49]. Bismuth (Bi), as an HER inert metal [58], is also widely studied for the CO$_2$RR in recent years. The Bi-based catalysts are demonstrated to be a selective and active for the HCOOH production [48]. Due to the low cost and low toxicity, Bi becomes as important as Sn and is to be used in large-scale CO$_2$RR to HCOOH [59].

3.2 Metal sulfides

In very recent years, sulfur-modified metals have been explored as electrocatalysts, showing promising catalytic performance for the CO$_2$RR. Cu$_x$S is one of the most intensively studied sulfides, which can selectively produce HCOOH [50]. SnS$_x$ [51], PbS$_x$ [56], BiS$_x$ [48] and InS$_x$ [55] are also demonstrated to be effective catalysts for the CO$_2$RR to HCOOH. Even though the promising performance, the role of S in the electrochemical performance is not clear until now. In order to design catalysts with higher activity, selectivity and stability, it is necessary to acquire a deeper understanding of how S functions during CO$_2$RR by performing both in-situ/operando experiments and theoretical studies.

3.3 Bimetallic catalysts

Compared with the pure metals, bimetallic catalysts with tuned electronic and structural properties are of particular interest. Early studies by *Hori* et al. [57] have shown that the modification of metallic surface with foreign atoms can tune the selectivity for CO or HCOO$^-$ production. Sn-based bimetallic materials are the most studied type, probably due to the high performance of Sn alone for the CO$_2$RR to HCOOH. It is worth to note that most of the Sn bimetallic materials show good HCOOH selectivity at very positive potentials, with much lower overpotentials with respect to those at the Sn/SnO$_x$ electrodes [56]. Particularly, a Cu-Au catalyst shows good selectivity and activity for the HCOOH production at even more positive potentials [54]. Until now, many studies suggested that the combination of different types of metals provide the opportunity to modulate the surface chemical
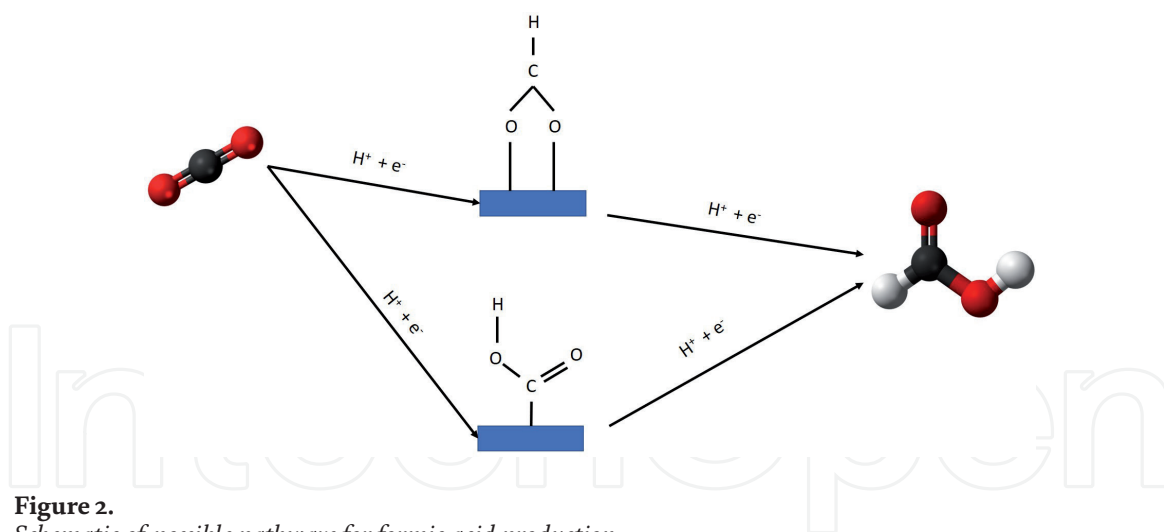
Figure 2.
Schematic of possible pathways for formic acid production.

environment and the relative binding with different intermediates, tuning the electrochemical performance of the multi-metallic catalysts in the CO_2RR.

In recent years, many works have been dedicated to understand the mechanism of the CO_2RR to $HCOOH$, including computational, electrokinetic and in situ analysis) [60–62]. As depicted in **Figure 2**, the formation of formate generally goes through the following pathway: 1) $CO_2 \cdot^-$ radical anion is firstly formed via a one-electron transfer and bonded to the electrode surface through O atom, 2) protonation of $CO_2 \cdot^-$ on the carbon atom leads to the formation of a $HCOO \cdot$ intermediate and 3) a second electron transfer and protonation step results in the $HCOOH$ product [63].

4. C_{1+} hydrocarbon selective electrocatalyst

The production of hydrocarbons through electrochemical reduction of CO_2 (a carbon-neutral fuel alternative to fossil fuels) is of interest because the infrastructure to store, transport and use methane and other hydrocarbons as fuel is already well established [64]. The major challenge for these products is to find the selective electrocatalysts to manage to reduce the CO_2 molecule with 8 and 12 electrons (methane and ethane). Considering the stability of the CO_2 molecule and the multi-electron-coupled-proton pathways, high energy barriers are needed to overcome for the formation of the intermediates and final product [48].

According to major reports, Cu-based materials are the main type of electrocatalysts that can produce hydrocarbon compounds including CH_4 and thus become the object under the most intensive study [65].

4.1 Cu alloys

Hirunsit et al. examined Cu_3X alloys by using computational methods to examine the electrochemical reduction to CH_4 [66]. In an important report, Kenis and co-workers recently reported the differences between ordered, disordered, and phase-separated Cu@Pd nanoparticles with respect to product selectivity [67]. Gewirth and co-workers showed that Cu-Ag alloys from additive-controlled electrodeposition exhibited ~60% FE for C_2H_4 in an alkaline flow electrolyzer. In this case, by tuning the Ag-loading an optimized C_2H_4 selectivity can be achieved. The Ag sites were believed to play the role of a promoter for CO formation during electrochemical CO_2 reduction [68].

4.2 Other metallic alloys

Although copper gained a lot of attention for hydrocarbon production through electrochemical reduction of CO_2, some other metallic alloys have also shown to be quite noteworthy for this application. For example, Lewis and co-workers reported nickel–gallium alloys of different compositions prepared by drop-casting and a subsequent temperature-programmed reduction method [69]. The alloy foil was slightly enriched in zinc both at the surface and in the bulk, with a surface alloy composition of 61.3 at% zinc and a predominantly Ag_5Zn_8 bulk phase. The FE_{CH4} values at 1.43 V vs. RHE were five times and three times higher with the alloys than those produced at pure Ag and Zn electrodes, respectively.

The summary of some recent reports for C_{1+} hydrocarbons are being reported in **Table 3**.

As for the possible pathways for electrochemical reduction of CO_2 to hydrocarbons, In an attempt to elucidate the mechanism of CO_2 reduction, it was found

Electrocatalyst	Electrolyte	Main Product	Potential (V vs. RHE)	Current Density ($-mA\ cm^{-2}$)	FE (%)	Reference
Cu nanowires/ rGO	0.5 M $KHCO_3$	Methane	−1.25	12	55	[70]
Cu-Porphyrin	0.5 M $KHCO_3$	Methane	−0.98	15	47	[71]
Pd decorated Cu	0.5 M $KHCO_3$	Methane	−0.96	57	46	[72]
CuS@Ni Foam	0.1 M $KHCO_3$	Methane	−1.1	7.3	73	[73]
Complex-derived Cu nanocluster	0.5 M $KHCO_3$	Methane	−1.06	19.7	66	[74]
n-Cu/C	0.1 M $NaHCO_3$	Methane	−1.35	10	76	[75]
Mesoporous Cu	0.1 M $KHCO_3$	Ethylene	−1.3	11.8	46	[76]
O_2-plasma-treated Cu	0.1 M $KHCO_3$	Ethylene	−0.9	12	60	[77]
Anodized-Cu	0.1 M $KHCO_3$	Ethylene	−1.08	19	38	[78]

Table 3.
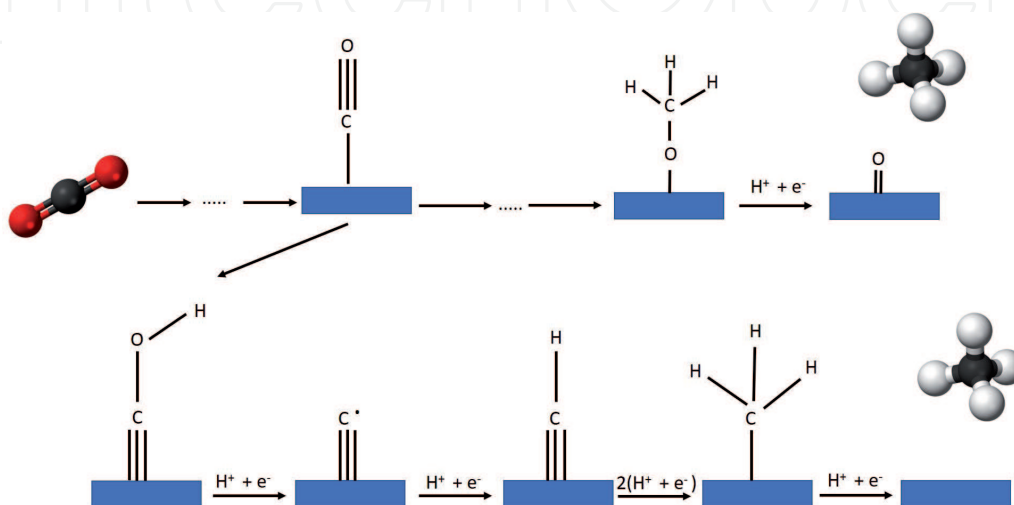*C_{1+} hydrocarbon selective electrocatalyst.*

Figure 3.
Schematic of possible pathways for methane production.

that CO is a key intermediate in the formation of CH$_4$ and C$_2$H$_4$ [79] and that the products of CO$_2$ reduction reaction depend on the metal's binding energy to CO [80]. Based on these findings, one strategy for efficient electrochemical CO2 conversion is to separate the process into two steps: CO$_2$ reduction to CO, followed by CO reduction to oxygenates and hydrocarbons [81]. The schematic of the possible pathways toward methane production has been illustrated in **Figure 3**.

5. Oxygenated alcohol selective electrocatalysts

The wide range of theoretically possible products from CO to C$_{2+}$ alcohols and hydrocarbons and fuels makes the recent research to put a lot of efforts on production of more valuable products like oxygenated alcohols. The major problem as discussed before is due to a very stable structure of CO$_2$ molecule, very high activation energy needed to transform it to more attractive molecules. This high activation barrier would cause high over potentials and in case of oxygenated alcohols like methanol or ethanol high numbers of electrons (6 and 12 respectively) needed to reduce CO$_2$ molecule to desired products. So far many different metallic and alloys have been used as electrocatalysts for this application [82]. Although the performance of other product formations such as CH$_3$OH and C$_2$H$_5$OH were well below the target values, the market size of these chemicals was estimated to be much larger than those of HCOOH and CO [83]. Thus, the co-production of economically viable HCOOH and CO with other products such as CH$_4$,C$_2$H$_4$,CH$_3$OH, and C$_2$H$_5$OH was suggested to cancel out the maximum voltage requirement [84].

5.1 Metal alloys

Of all metals, Cu has been identified as unique in that it is able to produce a number of "beyond CO" products such as hydrocarbons and organic oxygenates such as aldehydes and alcohols [85]. Moreover, metal alloys can adjust the binding ability of active intermediates and thus are promising to enhance the reaction selectivity and kinetics. Lu et al. [21] have synthesized an aerogel with high porosity when [BMIM][BF$_4$] and H$_2$O with a molar ratio of 1:3 were selected as electrolytes, the faradaic efficiency (FE) and current density of CH$_3$OH can be up to 80% and 31.8 mA/cm^2, respectively, over the Pd$_{83}$Cu$_{17}$ aerogel which attributed to the valence states, ratios, and strong interaction of Pd and Cu [86]. Also, a Zn/Ag foam electrocatalyst was prepared by Low et al. The active sites in this electrocatalyst are the strained submicron Zn dendrites, resulting in a FE of 10.5% for producing CH$_3$OH [87].

5.2 Metal oxides

Metal oxide electrocatalysts have the merits of high selectivity and high energy efficiency [88]. Cuprous oxide/polypyrrole particles with octahedral and icosahedra structure (Cu$_2$O(OL-MH)/Ppy) can achieve a ultrahigh CH$_3$OH activity and selectivity with FE of 93 ± 1.2% and 1.61 ± 0.02 μmol/(cm^2·s) formation rate at −0.85 V [89]. Albo and Irabien [90] used gas diffusion electrode loaded with Cu$_2$O and achieved a FE of 42.3% for CH$_3$OH formation, founding that Cu + can significantly affect the selectivity and activity toward CH$_3$OH. Moreover, nano Cu$_2$O has a higher stability and selectivity compared with Cu for CH$_3$OH production. The result of more metallic alloys and metal oxide electrocatalysts for this application have been illustrated in **Table 4**.

Electrocatalyst	Electrolyte	Main Product	Potential (V vs. RHE)	Current Density ($-mA\ cm^{-2}$)	FE (%)	Reference
Cu$_2$O/ZnO	0.5 M KHCO$_3$	Methanol	−0.7	6.8	17.7	[91]
Pd/SnO$_2$	0.5 MNaHCO$_3$	Methanol	−0.24	1.45	54.8	[82]
Cu modified Pd	0.5 M KHCO$_3$	Methanol	−0.46	0.5	19.5	[92]
Cu nanoparticle/ N-doped graphene	0.1 M KHCO$_3$	Ethanol	−1.2	0.7	63	[93]
B-and-N-co-doped Nanodiamond	0.1 M KHCO$_3$	Ethanol	−1	1	93	[94]
Cu$_2$O films	0.1 M KHCO$_3$	Ethylene and Ethanol	−0.99	35	34.3 and 16.4	[95]

Table 4.
Oxygenated alcohol selective electrocatalysts.

It is noteworthy to mention that there are different pathways suggested for methanol and ethanol production via electrochemical reduction of CO$_2$. One possible pathway for methanol production is believed to be produced through hydrogenation of methoxy intermediate (*OCH$_3$) [44]. In detail, the *CO species is formed first. Then, the *OCH$_3$ intermediate is made from the competition between desorption of formaldehyde and the proton electron coupled transfer to formaldehyde bonded on local surface. At least, another proton electron coupled transfer occurring on *OCH$_3$ species results in methanol [65]. This possible pathway has been illustrated in **Figure 4**. In addition, the plausible pathway for ethanol
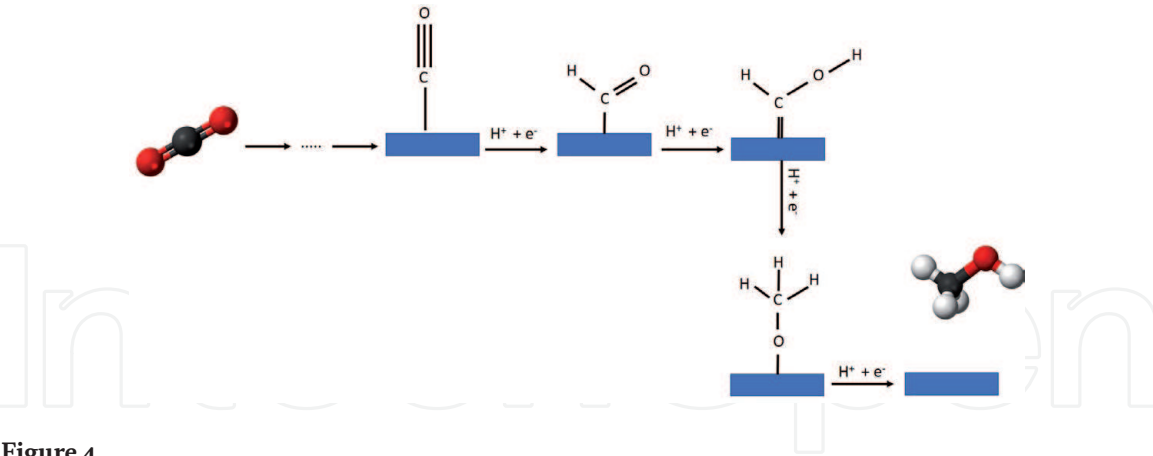

Figure 4.
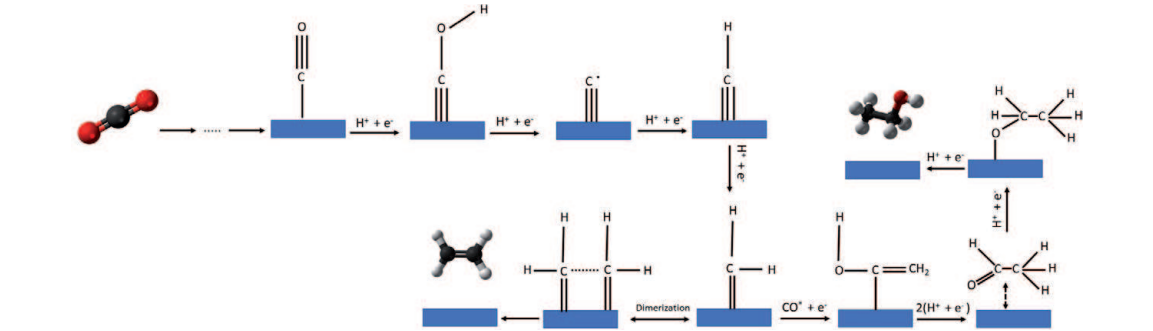*Schematic of possible pathways for methanol production.*

Figure 5.
Schematic of possible pathways for ethylene and ethanol CO production.

production should be discussed alongside ethylene. Ethylene is generally believed to form through either dimerization of *CH$_2$ species or proton electron coupled transfer to the carbon site of the ethylene oxide intermediate (*OCHCH$_2$) that is derived from dimerization of *CO [79]. Both routes might be the halfway leading to formation of ethanol by insertion of *CO species into *CH$_2$ species or proton electron coupled transfer to the oxygen site of the *OCHCH$_2$ species, correspondingly [65], as illustrated in **Figure 5**.

6. Conclusions

In this chapter different electrocatalysts for electrochemical reduction of CO$_2$ to value added products have been discussed. A wide range of molecules from CO and HCOOH to hydrocarbons and oxygenated alcohols are possible products of this electrochemical reaction. Up to this date the main challenge of these electrocatalytic reactions remains on scaling up and eventually industrializing the production of these value added products. The main drawback of these electrocatalytic reactions are their relatively high overpotentials and low production rate for scaling up. Although the prospective of this technology are bright, the main effort still is to find the stable, abundant electrocatalyst to be used for efficient electrocatalytic reduction of CO$_2$ at industrial scale.

Author details

M. Amin Farkhondehfal* and Juqin Zeng
Center for Sustainable Future Technologies (CSFT@POLITO), Istituto Italiano di Tecnologia, Turin, Italy

*Address all correspondence to: amin.farkhondehfal@iit.it

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