

## Electrocatalytic reduction of CO<sub>2</sub> into useful chemicals-A Brief Review

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### Abstract

Electro reduction of CO<sub>2</sub> has become a subject of great importance over the last few decades. This is fundamentally because CO<sub>2</sub> is a notorious green house gas released both by artificial and natural processes. This review highlights current status and future directions in the electroreduction of CO<sub>2</sub> into sustainable production of useful fuels. The current trends in understanding of CO<sub>2</sub> reduction process and the pathways through which various products are formed are discussed. Electro Catalysts play a very important role in the CO<sub>2</sub> reduction process to generate low-carbon fuels, including CO, HCOOH/HCOO<sup>-</sup>, CH<sub>2</sub>O, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>/HC<sub>2</sub>O<sub>4</sub><sup>-</sup>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH and others. The electro-catalysts can be classified into several types, which include metals, metal oxides, metal alloys, metal complexes, polymers/organic molecules and others. The vital characteristics of electro-catalysts which include product selectivity, activity, Faradaic efficiency and catalytic stability have been discussed in detail. The experimental evidence available so far indicates copper is the best catalyst for electroreduction of CO<sub>2</sub> into hydrocarbons. In particular, recent developments showing high selectivity and faradaic efficiency for generation of ethanol in oxygen derived copper nanoparticles as well as copper nanoparticles supported on carbon nano-spikes are extremely interesting. The review also presents basic aspects of electrochemical cell for the electroreduction of CO<sub>2</sub>. Finally, the demonstration of feasibility of a two step CO<sub>2</sub> conversion into liquid fuels and the challenges in developing highly active and stable electro-catalysts for reduction of CO<sub>2</sub> are discussed, indicating directions for future research and development in this very important area.

**Keywords:** CO<sub>2</sub> conversion, CO<sub>2</sub> reduction, Copper, Ethanol, electro-catalysis, Reaction mechanism.

### 1 Introduction

The electrocatalytic conversion of carbon dioxide (CO<sub>2</sub>) into useful chemicals has attracted many researchers worldwide for decades as it can enable a sustainable low temperature redox cycle for energy conversion and storage [1, 2]. While CO<sub>2</sub> is an essential substance for the growth of all plants and for numerous industrial processes, it has now become a significant greenhouse gas due to both natural and manmade processes [3-6]. In an ideal situation, CO<sub>2</sub> consumed should be balanced with what is produced on Earth, so that the level of CO<sub>2</sub> remains constant to maintain environmental stability. However, increased human industrial activities and consumption of fossil fuels has caused imbalance in CO<sub>2</sub> concentration in the environment and has made global warming an urgent issue. Hence, reduction of CO<sub>2</sub> production and conversion of excess CO<sub>2</sub> into useful chemicals is critical, for environmental protection. Therefore, various governments all over the world have shown concern by increasing their funding for research to address the CO<sub>2</sub> issue. Hence, electrochemical reduction of CO<sub>2</sub> into useful products and chemicals is urgently needed [7,8]. However, Carbon dioxide (CO<sub>2</sub>) produced by most hydrocarbon feedstock combustion processes is a thermodynamically stable product [9] and hence, reduction of CO<sub>2</sub> is challenging.

During the last 30 years a great deal of research effort has been directed in the electrochemical reduction of CO<sub>2</sub>. Electrochemical conversion of CO<sub>2</sub> into hydrocarbons was reported in 1985 by Hori et al. using cathode materials such as Cd, In, Sn and Pb which predominantly gave formate and small amount of CO, CH<sub>4</sub> and H<sub>2</sub>. More importantly, they reported the production of CH<sub>4</sub> on pure copper as a cathode for the first time [10]. In 1986, the same authors reported the production of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> by electrochemical

reduction of CO<sub>2</sub> at Cu electrode in aqueous KHCO<sub>3</sub> solution [11]. Later in 1988 J. J. Kim et al. reported that the onset potentials of ethene and methane were -1.5 to -1.6 V vs. saturated calomel electrode (SCE) and demonstrated that CH<sub>4</sub> is formed from CO at a rate 50 times lower than from CO<sub>2</sub> with an onset potential of -1.5 to -1.6 V vs. saturated calomel electrode (SCE). The methane formation rate was higher if the surface was prepared by cleaning with HCl rather than HNO<sub>3</sub>, or oxidation in air [12]. In 1989, Y. Hori et al. studied electrocatalytic conversion of CO<sub>2</sub> in aqueous inorganic electrolytes at Cu electrodes by means of coulometric, chronopotentiometric, and voltammetric measurements and reported the production of CO, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, Ethanol and Pr<sub>n</sub>OH at ambient temperatures. They reported that pH at the electrode is significantly affected by the electrolyte, due to the formation of OH<sup>-</sup> at the electrode [13]. Y. Tomita et al. (2000) have investigated electrochemical reduction of CO<sub>2</sub> at platinum electrode at 5 mA/cm<sup>2</sup> current density in 0.1 M tetraethylammonium perchlorate acetonitrile-water mixtures. They reported that Pt can reduce CO<sub>2</sub> primarily to oxalic acid in anhydrous acetonitrile. They observed that the yield of formic acid increased and the oxalic acid formation dropped with the increase of water concentration. With further increase of water concentration CO<sub>2</sub> reduction was suppressed and hydrogen evolution prevailed. They found that Pt electrode covered with CO behaves like the Pb electrode [14]. Takahashi et al. (2002) have reported electrochemical conversion of CO<sub>2</sub> using two series of crystalline electrodes, Cu(S)-[*n*(111) × / (111)] and Cu(S)- [*n*(110) × / (100)] at 5 mA cm<sup>-2</sup> constant current density in 0.1M KHCO<sub>3</sub> aqueous solution. Using 99.999% copper metal, crystalline copper was grown in a graphite crucible, and X-ray back reflection method was used to determine the crystal structure. The product distribution of CO<sub>2</sub> reduction was found to vary substantially with the crystal orientation. Electroreduction of CO<sub>2</sub> at the Cu(110) = Cu(S)-[2(111) × (111)] yields 20% of CH<sub>3</sub>COOH and the yield of CH<sub>4</sub> was only 6% at the Cu(110) electrode. The production of CH<sub>3</sub>COOH and CH<sub>4</sub> changed substantially with the crystal orientation [15].

A. A. Peterson et al. (2010) have given a theoretical basis using density functional theory (DFT) calculations, which explains unique ability of copper to convert CO<sub>2</sub> into useful fuels, which may lead to (photo-) electrochemical routes for the generation of fuels [16]. K. J. P. Schouten et al. (2011) have proposed a novel mechanism for the electrochemical reduction of CO<sub>2</sub> on Cu electrodes. They show that CHOCO<sub>ads</sub> is the key intermediate in the breaking of the C-O bond and, hence, in the production of CH<sub>4</sub>. It is also suggested that for the production of C<sub>2</sub>H<sub>4</sub>, the first step is the generation of a CO dimer, followed by the generation of an enediolate or enediol, or the generation of an oxametallacycle. In contrast to previously proposed Fischer-Tropsch-like mechanisms, both the oxametallacycle

and the enediol(ate) would explain the observed selectivity of C<sub>2</sub> pathway for the formation of C<sub>2</sub>H<sub>4</sub> [17]. New insights were reported recently by K.P Kuhl et al. about the electrochemical conversion of CO<sub>2</sub> on a Cu surface, which was facilitated by an experimental method with excellent sensitivity for identifying and quantifying carbon dioxide electroreduction products. They studied Cu at different potentials and observed 16 different carbon dioxide reduction products [18].

J. H. Montoya et al. (2013) have presented a theoretical study of C-C coupling in carbon dioxide electroreduction on the Cu (211) surface. They studied kinetic barriers to the formation of a carbon-carbon bond between adsorbates derived from CO using DFT calculations. Their results demonstrate that kinetic barriers to carbon-carbon coupling decrease substantially with the level of hydrogenation of reacting adsorbates. They showed that the chemical potential of H<sub>2</sub> can be changed through the applied potential in the electrochemical environment, which leads a variation of the level of hydrogenation of the reactant chemicals, and thus the activation barrier for C-C coupling [19]. W. Zhu et al. (2013) have studied selective electrocatalytic conversion of CO<sub>2</sub> to CO on Au nanoparticles in 0.5 M KHCO<sub>3</sub> at 25°C [20]. In another experiment, D. Kim et al. (2014) have found that the factors related to the geometric effect, intermediate binding, and the electronic effect, controls the activity of bimetallic Au-Cu nanoparticles. Great mass activities are also shown by these nanoparticle monolayers, outperforming conventional CO<sub>2</sub> reduction catalysts. They opined that the insights gained through their study can serve as a basis for designing better CO<sub>2</sub> electrochemical conversion catalysts [21]. K Manthiram et al. (2014) have demonstrated that glassy carbon supported Cu nanoparticles (n-Cu/C) can realize up to 4 times better methanation current densities as compared to electrodes of high-purity Cu foil. The n-Cu/C electrocatalyst also shows an average Faradaic efficiency for 80% methanation during long electrolysis, which is the highest Faradaic efficiency reported at room-temperature methanation. They have found that the level of Cu catalyst loading on the glassy carbon support has a significant effect on the surface morphology of Cu under catalytic conditions and the consequent Faradaic efficiency for CH<sub>4</sub> [22].

R. Kas et al. (2014) have reported the generation of C<sub>2</sub>H<sub>4</sub> in CO<sub>2</sub> electro-reduction over rough Cu electrodes and explained that it is due to the presence of specific surface morphology. They demonstrated that similar electrode coated with Cu nanoparticles can give either methane or ethylene, depending on the applied CO<sub>2</sub> pressure and electrolyte concentration. Their pH calculation near the electrode surface shows that high local pH favors ethylene formation. Also, the conditions leading to the generation of CH<sub>4</sub> cause rapid reduction of hydrocarbon formation rates, and electrode performance can be sustained for

hours in conditions favoring ethylene production. This study significantly changes the mechanistic interpretation of ethylene generation over rough Cu surfaces and shows that process conditions causing pH variations close to the surface of the electrode need to be considered [23]. Using DFT calculations D. H. Lim et al. (2014) have demonstrated that defective graphene-supported Cu nanoparticles can change the electronic and structural properties of Cu for increasing electrochemical conversion of CO<sub>2</sub> into useful fuels. This paper provides better understanding of CO<sub>2</sub> reduction mechanisms on both Cu and the Cu nanoparticle systems and explains factors responsible for enhanced CO<sub>2</sub> conversion [24]. H. Li et al. (2014) have identified the ensemble site for bond making and bond breaking on (100) surfaces as a site consisting of two opposing bridge sites, i.e., a double-bridge ensemble site, based on extensive DFT calculations of the mechanisms of dimethyl ether oxidation on platinum, carbon monoxide reduction on copper, ammonia oxidation on platinum, and oxygen reduction on gold. The existence of this site explains why these reactions all prefer the (100) terrace and why steps and defects in the (100) surface lower the activity. Their work gives a fundamental understanding for a particular type of structure sensitivity in heterogeneous (electro)catalysis involving the making or breaking of bonds between carbon, nitrogen and/or oxygen. Such unusual structure sensitivity is responsible for significant deviations in well-known scaling laws, which opens up the pathway for the design of superior heterogeneous catalysts [25]. Recently J. Wei et al. (2017) reported an efficient, highly stable and multifunctional catalyst comprising of nanocrystalline HZSM-5 zeolite and Na-Fe<sub>3</sub>O<sub>4</sub> nanocatalyst. They reported that this catalyst can convert CO<sub>2</sub> to gasoline-range (C5-C11) hydrocarbons directly with CO<sub>2</sub> conversion efficiency of 22% and selectivity ~ 78% under industrial relevant conditions [26].

The particle size effect has been investigated by R. Reske et al. (2014) for the catalytic electroconversion of CO<sub>2</sub> on 2-15 nm Cu nanoparticles and compared to bulk Cu. Nanometer-sized Cu nanoparticles exhibited a drastic enhancement in overall catalytic activity. Study of selectivity has shown that increased formation of CO and H<sub>2</sub> accounts for the enhancement in the faradaic activity seen on the copper nanoparticles. The selectivity of hydrocarbons initially changed to a reduced plateau, till it virtually disappears for nanoparticle sizes at and below 2 nm [27]. R. Kortlever et al (2015) have shown that Pd<sub>x</sub>Pt(100<sub>x</sub>)/C nanoparticles have a reduced onset potential for the formation of CH<sub>2</sub>O<sub>2</sub> from CO<sub>2</sub>, with good selectivity. They showed the faradaic efficiency for the generation of formic acid can be very high for the Pd<sub>70</sub>Pt<sub>30</sub>/C nanoparticles depending on their composition [28]. In another paper, they have discussed design strategies for the development of selective and efficient catalysts for the electro-catalytic conversion of CO<sub>2</sub>. One of these strategies

is the alloying of different metals in order to optimize the binding energies of reaction intermediates like COOH<sub>ads</sub>. Alloying might also be good for breaking scaling relations between similarly adsorbed intermediates as they cause intrinsic adsorption overpotentials. Additionally, product selectivity can be influenced by the pH of the electrolyte and the use of nonaqueous electrolytes instead of aqueous electrolytes. Therefore, optimal CO<sub>2</sub> reduction systems require the conjunction of a catalyst with suitable adsorption properties and an electrolyte with beneficial effects on the catalytic activity and selectivity [29]. Au@Cu core-shell nanoparticles having well-defined surface structures have been evaluated by J. Monz et al (2015), as catalysts for the electrochemical conversion of CO<sub>2</sub> in neutral medium [30]. J. Rosen et al (2015) have reported computational and experimental methods to investigate the electrocatalytic reaction mechanism of carbon dioxide reduction on nanostructured silver catalyst surfaces. They found that both nanoparticle and nanoporous Ag catalysts show enhanced ability to reduce the activation energy of the CO<sub>2</sub> to COOH<sub>ads</sub> reaction in comparison to bulk Ag catalysts [31]. E. Bertheussen et al in 2016 have reported that acetaldehyde is an intermediate in the electro-reduction of CO to C<sub>2</sub>H<sub>5</sub>OH on oxide-derived Copper. They found that oxide-derived copper (OD-Cu) electrodes show excellent CO reduction ability for hydrocarbons, forming acetate and ethanol with >50% Faradaic efficiency at -0.3 V (vs.RHE). They identified acetaldehyde as a smaller product but a key intermediate in the electro-reduction of CO to C<sub>2</sub>H<sub>5</sub>OH on OD-Cu electrodes using chromatography [32]. Stressing the carbon energy cycle, CO<sub>2</sub> + energy → methane → CO<sub>2</sub> + energy, M. Gattrell et al. (2006) [33] have emphasized that the synthesis of hydrocarbons from carbon dioxide is a complex multistep reaction process with mainly adsorbed CO intermediates. They have also stated that the reaction product distribution is very sensitive to the surface crystal structure of Cu electrode.

Very recently, Y. Song et al. Oak Ridge National Laboratory (2016) reported an electrocatalyst which operates in water at room temperature for the electro-conversion of dissolved CO<sub>2</sub> with better selectivity for ethanol. Their experiment shows that multiple reactive sites on nanostructured surfaces in close proximity can give novel reaction mechanisms leading to high selectivity for a 12-electron reaction. This indicates that the synergistic effect from interactions between copper and carbon nanospikes presents a novel strategy for developing highly selective electrocatalysts. This path-breaking work by Y. Song et al. that produces ethanol from CO<sub>2</sub> with 63% conversion efficiency could be an important pathway towards creating a low-carbon energy system [34-36].

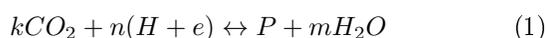
However, many major issues still need to be addressed before the electrocatalytic conversion of CO<sub>2</sub> into

useful chemicals becomes cost-effective for technological applications. The main problems faced today in electrocatalytic CO<sub>2</sub> conversion are the high overpotentials needed and the poor product selectivities and faradaic efficiencies. The poor product selectivities and high overpotentials are mainly due to inappropriate adsorption energies of key reaction intermediates which are mediated by catalysts [37, 38, 16]. Further, the competing hydrogen evolution reaction (HER) which occurs in the same range of potentials as that of CO<sub>2</sub> conversion results in low faradaic efficiencies [39, 40]. Thus, catalysts need to be explored to increase the efficiency of electrocatalytic CO<sub>2</sub> conversion and product selectivity while substantially lowering the overpotentials. However, CO<sub>2</sub> conversion into useful fuels is very challenging primarily due to the multiple number of proton-coupled electron transfer steps [41]. In this paper, a brief review of the electro-catalytic conversion of CO<sub>2</sub> into hydrocarbons based on work reported so far on the effect of structure of catalyst, design of electrochemical cell, electrolytic environment, temperature and other electro-catalytic conditions.

## 2 Reaction pathways

In order to understand the complex process of electrochemical CO<sub>2</sub> reduction, it is important to determine, both theoretical [17, 42] and experimental reaction mechanisms [16, 19, 37-38]. This will lead to more mechanistic insight, which will in turn, lead to better, tailor-made electro-catalytic systems. In this section, we will discuss the current trends in understanding of CO<sub>2</sub> reduction process and the pathways through which various products are formed.

The electrochemical conversion of CO<sub>2</sub> can be viewed as a multiple proton-electron reaction leading to various products and water as follows:



Where P represents 'product' in aqueous media, k, n, and m are the coefficients. Copper is currently the best-known metal catalyst for electrochemical conversion of CO<sub>2</sub> [33,44] capable of electrochemical conversion of CO<sub>2</sub> into more than 16 different products [18, 34] including CO, CH<sub>4</sub>, HCOOH, and C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>6</sub>, ethanol, allyl alcohol, n-propanol, acetaldehyde, propionaldehyde, acetate, ethylene glycol, methanol, glycolaldehyde, hydroxyacetone, acetone, glyoxal [18, 33, 43] and others depending upon electrode potential, pH of electrolyte, current density, catalyst surface structure etc. Table 1 gives some of the important products of electrochemical conversion of CO<sub>2</sub> with values of coefficients k, n and m provided in each reaction together with the standard equilibrium potentials.

Table 1: Major Products of the Electrochemical Reduction of CO<sub>2</sub>

Sl.No.	Product name and chemical formula	k	n	m	E <sup>0</sup>
1	carbon monoxide, CO	1	2	1	-0.10
2	formic acid, HCOOH	1	2	0	-0.20
3	formaldehyde, HCHO	1	4	1	-0.07
4	methanol, CH <sub>3</sub> OH	1	6	1	0.02
5	methane, CH <sub>4</sub>	1	8	2	0.17
6	ethanol, CH <sub>3</sub> CH <sub>2</sub> OH	2	12	3	0.09
7	ethylene, C <sub>2</sub> H <sub>4</sub>	2	12	4	0.08

In the past several years, many groups have studied the mechanism of the CO<sub>2</sub> conversion reactions [16, 17, 38, 45, 46]. It is understood that CO is an intermediate product in the conversion of CO<sub>2</sub>. DFT calculations show that chemical dimerization step of CHO or similar adsorbates leads to ethylene formation [16, 46]. Schouten et al. [17, 45] experimentally demonstrated that the Cu(100) surface offers a specially active reaction pathway for the generation of ethylene. The current major scientific challenges are controlling the selectivity of the carbon dioxide conversion reaction and reduction of over potential for the generation of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. The geometry, roughness and morphology, of Cu polycrystalline and single crystal surfaces have shown a strong effect on the product selectivity and catalytic activity during carbon dioxide electroconversion [47-49]. Increased C<sub>2</sub>H<sub>4</sub> and CO generation was reported on roughened copper foils [48]. The changed selectivity was explained based on changes in the chemisorption characteristics of (100), (111), and (211) surfaces of copper. Further, DFT studies showed that key intermediates like \*CO and \*CHO could be stabilized on stepped surfaces having more negative chemisorption energies [50].

Ever since Hori made his landmark discovery in 1985 that copper has the unique ability to electrochemically reduce CO<sub>2</sub> to hydrocarbons such as CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> with good faradaic efficiencies in comparison to other catalysts [10] substantial effort has been invested to understand the special reactivity of copper for this reaction [33]. As mentioned earlier, CO is an important intermediate in the production of hydrocarbons from the electro-conversion of CO<sub>2</sub> on copper, [51] which is generally accepted in the literature. However, proposing a conclusive mechanism for the conversion of CO<sub>2</sub> on Cu is challenging, as seen by the recent finding of 16 products formed from CO<sub>2</sub> [18]. Besides ethylene and methane, these products include a wide mix of ketones, carboxylic acids, aldehydes, and alcohols, out of which 12 are C<sub>2</sub> or C<sub>3</sub> species, showing the complexity of this reaction.

On the other hand, a carbene species (\*CH<sub>2</sub>) on the surface, formed from \*CO, was proposed to be a common intermediate for the production of methane and ethylene formation. Methane is then formed by double proton-electron transfer to the carbene intermediate, while ethylene is formed

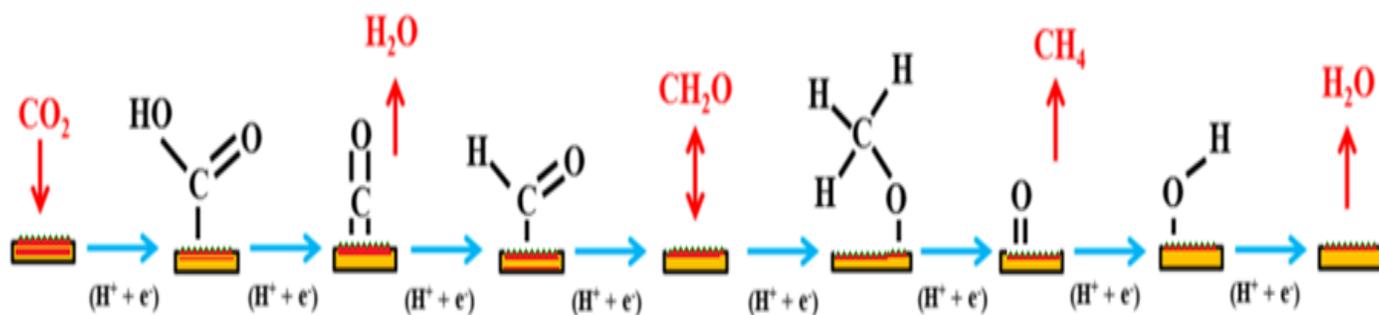


Figure 1: One possible pathway for the electrochemical formation of methane from  $\text{CO}_2$  on Cu electrodes; values of  $k$ ,  $n$  and  $m$  are 1, 8 and 2 respectively.

by either dimerization of  $^*\text{CH}_2$  species or addition of CO in a Fischer-Tropsch-like step, which has also been suggested to be the pathway for the formation of alcohols [52]. In contrast with this "carbene" mechanism, Peterson et al. have performed DFT calculations of the reduction of  $\text{CO}_2$  to methane on Cu (211) surfaces, suggesting that the thermodynamically most favorable pathway, and at a late stage of the mechanism, the second CO bond is broken as shown in Figure 1 [16]. After the initial formation of  $^*\text{CO}$ , there is subsequent hydrogenation to  $^*\text{HCO}$ ,  $^*\text{H}_2\text{CO}$ , and  $^*\text{H}_3\text{CO}$ , and this  $^*\text{HCO}$  intermediate is reduced to  $\text{CH}_4$  and  $^*\text{O}$ , which is later reduced to  $\text{H}_2\text{O}$ . Ethylene is produced by dimerization of  $\text{H} \times \text{CO}$  species and subsequent deoxygenation [19].

Although intensive experimental and theoretical studies have been carried out on electro-catalyst to understand the mechanism of electro-chemical  $\text{CO}_2$  reduction, the detailed mechanistic pathways are still uncertain. The important problems are: slow kinetics of  $\text{CO}_2$  electroreduction, even with high electrode reduction potentials applied on electro-catalysts; the low energy efficiency of the process; and high energy consumption. The biggest challenge recognized by researchers in  $\text{CO}_2$  electro-catalytic reduction is the insufficient stability and poor performance of the electro-catalysts. Hence, current research has to focus on promising metal catalyst such as copper with appropriate structure which will yield control of pathways and the production of useful hydrocarbons.

### 3 Role of electro catalysts

The number and quantity of each species present in an electrochemical cell strongly depend on the applied electrode potential, and type and selectivity of the electrocatalyst used. Most of the electro-catalysts used have insufficient selectivity, efficiency and stability. Most of the catalysts can survive for less than 100 hours [53-55]. This is much lower than the requirements for commercialization. Hence, unsatisfactory catalysis, which includes selectivity, low

catalytic activity and stability is the greatest challenge in  $\text{CO}_2$  electroreduction. During the past decades, most of the efforts in  $\text{CO}_2$  electroreduction studies have been directed on research and development efforts on electro-catalysts to solve the above challenges [56, 57]. This section specifically focuses on electro-catalysts for electroreduction of  $\text{CO}_2$  into useful hydrocarbons.

### 3.1 Electro-catalysts for $\text{CO}_2$ electroconversion

Transition metals, such as metal complexes are most commonly investigated electro-catalysts for  $\text{CO}_2$  electroreduction, since their active d electrons and vacant orbitals support the bonding between  $\text{CO}_2$  and metal for the formation of useful hydrocarbons and also facilitate the release of the reduction products through catalyst surface.

#### 3.1.1 Pt group metals

Electroreduction of  $\text{CO}_2$  on Pt electrode was investigated by Eggins and McNeill [58] in water,  $\text{CH}_2\text{CN}$ , propylene carbonate, and dimethyl sulfoxide (DMSO) solutions. Later, Brisard et al [59] studied the mechanism of  $\text{CO}_2$  electroconversion catalyzed by polycrystalline Pt in acidic media and found that the major product was  $\text{CH}_3\text{OH}$ . The surface morphology of single-crystal Pt electrodes has been found to have a substantial influence on catalytic activity for  $\text{CO}_2$  reduction [60, 61]. Centi et al [62] converted  $\text{CO}_2$  to hydrocarbons with long carbon-chain ( $> \text{C}_5$ ) at atmospheric pressure and room temperature in a continuous flow cell using carbon-supported nanoparticles of Pt (Pt/C) as the catalyst. Feng et al. [63] used a 3-D nano-structured porous electrode (nanoporous CuPt composites), for electroconversion of  $\text{CO}_2$  in ionic liquid BMIM.  $\text{BF}_4$  [63]. Recently, Pt/C-TiO<sub>2</sub> and Pt-Pd/C-TiO<sub>2</sub> nanocomposite cathodes were used to catalyze the electrochemical conversion of  $\text{CO}_2$  to  $\text{CH}_4$  and isopropanol [64]. Electroreduction of  $\text{CO}_2$  on various conductive oxide mixtures ( $\text{RuO}_2, \text{TiO}_2, \text{MOO}_2, \text{Co}_3\text{O}_4$ , and

Rh<sub>2</sub>O<sub>3</sub>) exhibited, high current efficiencies for CH<sub>4</sub> formation when the electrode potential was fixed close to the hydrogen evolution equilibrium potential in a solution of 0.2 M Na<sub>2</sub>SO<sub>4</sub> (pH 4) saturated with CO<sub>2</sub> [65]. Later, Bandi and Kuhne [66] studied the electrocatalytic performance of mixed Ru/Ti oxide electrodes; their results showed that increasing TiO<sub>2</sub> content leads to increase in the overpotential for H<sub>2</sub> evolution.

The electrocatalytic activity of Pd for CO<sub>2</sub> reduction was initially investigated in a 1.0M NaHCO<sub>3</sub> solution [67] which resulted in HCOOH and CO as major products. Further, small amounts of hydro-carbons evolved from a Pd electrode catalyzed electrolysis process in CO<sub>2</sub>-saturated KHCO<sub>3</sub> aqueous solution [68, 69]. It was found that CO yield increased significantly with increase of CO<sub>2</sub> pressure; with electrode potential at 1.8 V vs. Ag/AgCl in 0.1M KHCO<sub>3</sub>, the yield increased from 5.3% at 1.0 atm to 57.9% at 50 atm [69]. It was reported that the evolution of H<sub>2</sub> can be reduced by H<sub>2</sub> absorption on the Pd surface, and the absorbed H<sub>2</sub> can modulate the electro-catalytic activity, when it reacts with the adsorbed reaction intermediates [70]. In another experiment, it was showed that hydrogenated Cu-modified Pd electrodes have better catalytic activities, forming hydrocarbons such as HCOOH, CH<sub>2</sub>, and CH<sub>2</sub>OH [71, 72]. It has been reported that CO<sub>2</sub> electroreduction on Pd electrodes can take place at potentials more than the reversible hydrogen potential, indicating that adsorbed H<sub>2</sub> atoms may take part in the electroreduction of HCO<sub>2</sub><sup>-</sup> (CO<sub>2</sub>) to HCOO<sup>-</sup> [73]. The CO<sub>2</sub> electroreduction reaction on a Pd catalyst in a non-aqueous CH<sub>3</sub>CN solution was studied by Ohkawa et al [74] who compared the results with the results obtained in an aqueous solution and they showed that the concurrent desorption of H<sub>2</sub> could lead to increased catalytic activity for CO<sub>2</sub> electroconversion.

### 3.1.2 Molybdenum

Electrodes of tungsten and Molybdenum do not show significant activity towards CO<sub>2</sub> electro-reduction. Noda et al. (1996) [75] tested tungsten and Molybdenum electrodes in KCl- saturated 0.1 M KHCO<sub>3</sub> aqueous solution at 298°C at -1.6 V vs. Ag/AgCl, and did not find substantial catalytic activity for the electroconversion of CO<sub>2</sub>. However, in another study D. P. Summers et al. (1986) [76] used Mo metal electrodes in the electrolysis of CO<sub>2</sub>-saturated 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 4.2) at 20°C in -0.7 to -0.8 V potential range vs. saturated calomel electrode (SCE) and found greater than 50% Faradaic efficiency, with major product being CH<sub>3</sub>OH. Bandi et al [65] thermally decomposed a mixed metal oxide consisting of 45% TiO<sub>2</sub>, 30% MoO<sub>3</sub>, and 25% RuO<sub>2</sub>, on Ti foil to catalyze CO<sub>2</sub> electroconversion to CH<sub>4</sub>, but significant performance was not observed.

### 3.1.3 Titanium and Ruthenium

Titanium has no substantial catalytic activity towards CO<sub>2</sub> electroconversion [75]. However, TiO<sub>2</sub> has been found to show some activity in electroreduction of CO<sub>2</sub> [77, 78].

Electrocatalysis of CO<sub>2</sub> has also been tried with thin TiO<sub>2</sub> films or mixtures of TiO<sub>2</sub> and other metal oxides normally deposited on Ti metal. In the preparation of a CO<sub>2</sub> catalytic electrode, Monnier et al. [79, 80] prepared TiO<sub>2</sub>, TiO<sub>2</sub>-Ru (or RuO<sub>2</sub>), and TiO<sub>2</sub>-Pt thin films by thermal evaporation on Ti rods. Bandi et al. (1990) [65] deposited RuO<sub>2</sub>, TiO<sub>2</sub>, MoO<sub>3</sub>, Co<sub>2</sub>O<sub>4</sub>, and Rh<sub>2</sub>O<sub>3</sub> on Ti foil and showed that methanol and formic acid are major reduction products, as identified by gas chromatography. Electro-catalytic synthesis of low-density polyethylene (PE) was realized from CO<sub>2</sub> on a nano-structured TiO<sub>2</sub> (ns-TiO<sub>2</sub>) film in a mixture of 1-Ethyl-3-Methylimidazolium Tetrafluoroborate (EMIM.BF<sub>4</sub>) and H<sub>2</sub>O by controlled potential electrolysis at normal pressure and room temperature [81]. The ns-TiO<sub>2</sub> film appeared to be significantly efficient and selective for the electro-chemical reduction of CO<sub>2</sub> when EMIM.BF<sub>4</sub> was the solvent [81] as EMIM.BF<sub>4</sub> maintained a high concentration of CO<sub>2</sub> at the electrode surface. In another experiment, Qu et al. (2005) [82] loaded RuO<sub>2</sub> onto TiO<sub>2</sub> nanotubes (NTs) or nanoparticles (NPs) to form RuO<sub>2</sub>-TiO<sub>2</sub> (NTs) or RuO<sub>2</sub>-TiO<sub>2</sub> nanoparticles, which were later coated onto a platinum electrode for the electro conversion of CO<sub>2</sub>. The potentiostatic electrolysis of CO<sub>2</sub> on the RuO<sub>2</sub>-TiO<sub>2</sub> nanotubes coated platinum electrode showed 65.5% current efficiency for selective formation of CH<sub>3</sub>OH which is significantly better than was realised on the RuO<sub>2</sub>-TiO<sub>2</sub>(NP) coated Pt electrode.

### 3.1.4 Cobalt, Iron, and nickel

Electro-chemical reduction of CO<sub>2</sub> on Ni, Co, and Fe electrodes, in aqueous solutions under normal conditions forms some hydrocarbons along with CO and H<sub>2</sub>. These metals also have very significant activities for CO<sub>2</sub> and/or CO hydrogenation in heterogeneous catalytic reactions. At 30 atm, the electroconversion of CO<sub>2</sub> at a current density of 120 mA cm<sup>-2</sup> the Fe electrodes formed HCOOH with ~60% Faradaic efficiency [83]. Further, in the electro-conversion of CO<sub>2</sub> at nickel electrodes in aqueous media, H<sub>2</sub> and some hydrocarbons, such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, were produced. The Faradaic efficiency for CO<sub>2</sub> reduction on Ni electrodes could be enhanced by increasing the CO<sub>2</sub> pressure, polarizing the electrode potential at a more negative potential, and lowering the temperature [84]. In CO<sub>2</sub> electroconversion catalyzed by Ni and Fe electrodes, CO adsorption on these two metals was studied, and the results indicated that the bonding between CO and the metal surface was very significantly related to the catalytic activity [85].

### 3.1.5 Aluminum, gallium, indium, and thallium

Aluminum has been found to have low catalytic activity for CO<sub>2</sub> electroconversion [75, 86]. The reports show that for electrochemical reduction of CO<sub>2</sub> by aluminum electrode at -1.6 V vs. Ag/AgCl in 0.1 M KHCO<sub>3</sub> aqueous solution the Faradaic efficiencies for generation of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> were as small as 0.58%, 0.04%, and 0.11%, respectively,

with 99% for H<sub>2</sub> evolution [75]. In another experiment, high selectivity for CH<sub>3</sub>OH formation was observed at very high overpotentials using p-type Ga-containing semiconductors in a photo-electrochemical cell [87-89]. Further, Bocarsly et al. (2008) [90] reported the highly selective conversion of CO<sub>2</sub> to CH<sub>3</sub>OH at illuminated p-GaP electrodes, with Faradaic efficiency close to 100% for underpotentials larger than 300 mV at -0.52 V vs. SCE. CO<sub>2</sub> electroreduction at In electrode in aqueous media mainly forms formate [10, 91, 92], but in nonaqueous solutions, the major product is CO [92]. Kapusta and Hackermant [91] also reported ~95% current efficiency in a 0.5 M HCOOH + 0.5 M HCOONa solution for CO<sub>2</sub> conversion to formate. Further, the conversion of CO<sub>2</sub> to formate was studied by Narayanan et al [93] in an alkaline polymer electrolyte membrane cell with Indium powder-coated porous carbon paper as cathode electrode. For the cathode feed, three different aqueous solutions (CO<sub>2</sub>-saturated deionized H<sub>2</sub>O, 1 M NaHCO<sub>3</sub>, and 1M Na<sub>2</sub>CO<sub>3</sub>) were used. The instantaneous Faradaic efficiency of formate production achieved in NaHCO<sub>3</sub> solution was as high as 80% initially and it decreased to ~ 10% over a period of 1.0 hour. Carbon mass transport was observed to be the factor limiting Faradaic efficiency. This mass transport limitation can be reduced using high carbon dioxide pressure or high bicarbonate concentration leading to stable operation with high Faradaic efficiency even at moderately high current densities. On the other hand, Tallium electrodes in aqueous electrolyte solution have been observed to increase the production of HCOOH, while in nonaqueous solutions, C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> has been found to be the major product [92,94].

### 3.1.6 Silver, gold, zinc and cadmium

When appropriate electrolytes are used both Au and Ag metals show significant catalytic activity towards CO<sub>2</sub> electroconversion [95]. The Faradaic efficiencies for CO production during CO<sub>2</sub> electroreduction at Au(99.95%) and Ag(99.98%) metals in 0.1M KHCO<sub>3</sub> aqueous solution at 25°C, at -1.6 V vs. Ag/AgCl saturated with KCl solution were observed to be 81.5%, and 64.7% respectively [75]. Further, it was reported [96] that when nanoporous Cu composites (NPC) coated with silver were used in CO<sub>2</sub> electroreduction in BMIM.BF<sub>4</sub> as electrolyte, dimethyl carbonate (DMC) could be electro-synthesized with a high yield of 80% which was attributed to the large surface area with open porosity and large efficiency of silver coated NPC composite electrodes. Sputter-deposited thin film Au electrodes have been used for CO<sub>2</sub> electroreduction [97]. The results showed that Argon pressure had an influence on the geometrical structure of surface area of Au surface, resulting in different CO<sub>2</sub> reduction potentials in both KCl and KHCO<sub>3</sub> solutions. A porous gold film electrode prepared by vapor deposition was also used for the electroconversion of CO<sub>2</sub> to CO in 99.99% KHCO<sub>3</sub> aqueous solution [98]. Zn and Cd electrodes were considered as suitable electrodes for CO<sub>2</sub> reduction due

to their high overpotentials for hydrogen evolution.

Reports show that electro-catalytic reduction of CO<sub>2</sub> on Zn and Cd electrodes in 0.1M KHCO<sub>3</sub> aqueous solution was found to have good selectivity for the formation of HCOOH and CO. On metallic Zn and Cd electrodes, the Faradaic efficiencies of HCOOH were found to be 20% and 39%, while those of CO were 39.6% and 14.4%, respectively [75]. Shibata et al. [99] employed a Cd-loaded gas diffusion electrode to reduce CO<sub>2</sub> and nitrite ions with various catalysts and observed that the maximum current efficiency for urea ((NH<sub>2</sub>)CO) production was ~55% at -1.0 V vs. SCE.

### 3.1.7 Tin and lead

Tin electrodes were found to be very active towards CO<sub>2</sub> electroconversion forming HCOO<sup>-</sup> in aqueous electrolytes, but the major product was CO, with small quantity of glyoxalic acid, oxalic acid, and formic acid in nonaqueous electrolytes [92, 94]. Some reports show that, Tin working electrode could catalyze CO<sub>2</sub> electro-conversion in aqueous inorganic salt solutions to form formic acid with a high current efficiency ~95% [10, 91]. However, organometallic complexes produced on the electrode surface during the reduction reaction process led to accelerated hydrogen evolution and consequent poor reaction efficiency [91].

Increase of temperature caused a reduction in Faradaic efficiency for HCOOH formation and an increase for H<sub>2</sub> production [100]. Li and Oloman [101, 102] used a granulated tin cathode with 99.9 wt% Sn and a CO<sub>2</sub> feed gas in a new reactor system and showed that the granulated tin cathode gave higher performance than the Sn-Cu mesh cathode reported by them earlier, in terms of both current efficiency and stability [101, 103].

Using Sn<sup>0</sup> and SnO<sub>x</sub> thin-film catalyst prepared by electrodepositing onto a Ti electrode, and CO<sub>2</sub> - saturated aqueous NaHCO<sub>3</sub> solution, Chen and Kanan [104] showed that Sn<sup>0</sup>/SnO<sub>x</sub> catalyst showed upto eight-fold higher partial current density and four-fold higher Faradaic efficiency for CO<sub>2</sub> conversion, more than that for tin metal coated with a native SnO<sub>x</sub> layer. They indicated that metal-metal oxide composite electrodes are better catalysts for generation of hydrocarbons. CO<sub>2</sub> electroreduction was carried out using Pb electrode at -1.5 to -2.2 V vs. NHE in aqueous solutions of ammonium salt, with a carbonate/bicarbonate buffer which was required to maintain 8.3 pH [105]. Pb catalyst in aqueous electrolytes predominantly formed HCOOH; in non-aqueous electrolytes, C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> was the dominant product [92].

Decreasing the temperature and increasing the CO<sub>2</sub> pressure increased Faradaic efficiency on Pb electrode [106]. With a high pressure of ~50 atm and a high temperature of ~80°C, Pb granule electrodes with aqueous 0.2M K<sub>2</sub>CO<sub>3</sub>

electrolyte solution, resulted in major reaction product formic acid, with a high Faradaic efficiency of 94% at -1.8 V vs. SCE [107]. On the other hand, CO<sub>2</sub> electroconversion carried out at normal pressure and temperature, resulted in CO and CH<sub>4</sub> among other products [107].

### 3.1.8 Alkaline metals and Other catalysts

Alkaline metals including alkaline earth metals cannot be utilized as catalysts for CO<sub>2</sub> electro-conversion due to their instability in electrochemical systems. Nevertheless, the salts of alkaline metals generally used for CO<sub>2</sub> electro conversion, as supporting electrolytes in electrochemical cells, exhibit different effects on reaction rate, product selectivity and catalyst stability. Organic molecules can also function as mediators and catalysts for CO<sub>2</sub> electroconversion other than the metals and metal complexes [108].

Some conducting polymers have also been utilized for the heterogeneous electrocatalysis of CO<sub>2</sub> electroconversion such as poly-aniline (PAN); the maximum Faradaic efficiencies were observed to be 12% for HCOOH and 78% for CH<sub>3</sub>COOH in CH<sub>3</sub>OH solution [109]. In another experiment, a polypyrrole (PPy) electrode developed by Aydin et al. [109] was used in the electro-catalytic reduction of CO<sub>2</sub> under high pressure in CH<sub>3</sub>OH at an overpotential value of -0.4 V vs. Ag/AgCl and the maximum Faradaic efficiencies found at 20 bar were 1.9, 40.5, and 62.2% for HCHO, HCOOH, and CH<sub>3</sub>COOH, respectively.

## 3.2 Copper and Oxidized Copper

Ever since Hori et al made their landmark discovery in 1985 that copper has the unique property as an electro-catalyst to reduce CO<sub>2</sub> to useful fuels such as CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> with better faradaic efficiencies in comparison to other catalysts [10], substantial effort has been directed to understand the special reactivity of Cu for this reaction [33]. CO was shown to be the key intermediate in the production of hydrocarbons from the electro-conversion of CO<sub>2</sub> on Cu [110], which is now widely accepted in the literature. Copper is the most important electrode capable of catalyzing the production of substantial quantity of hydrocarbons at high reaction rates over sustained periods of time; however, high over-potentials are required during electro-reduction and a fairly broad mix of major and minor hydrocarbons are formed [10]. Hence, proposing a conclusive mechanism for the electro-conversion of CO<sub>2</sub> on Cu is a challenging task [18]. Nevertheless, an insight into its unique ability to catalyze the formation of hydrocarbon would help in the synthesis of novel catalysts that are active at a lower over-potential and with better product control and simultaneously with good stability.

While a detailed theoretical understanding of various factors influencing electrochemical reduction of CO<sub>2</sub> is required, significant progress has been achieved during

the last few years in the development of new electro-catalysts based on copper which have greatly enhanced both selectivity and Faradaic efficiency for the generation of useful hydrocarbons.

The Copper electrodes so far developed are classified into different types of electrodes: bulk Cu, in situ electrodeposited Cu, Cu-electrodeposited GCE [10, 111, 112], Cu-coated GDE [113], Oxygen derived copper and Copper nanoparticles, and copper nanoparticles on N-doped Graphene [34]. Apart from the low hydrocarbons such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, CO, HCOOH, alcohols (methanol, CH<sub>3</sub>CH<sub>2</sub>OH, and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH), and esters, some relatively high hydrocarbons-such as olefins and paraffins having up to 6 carbon atoms-can also be produced using copper electrodes [10, 11, 13, 75, 96, 114, 115]. The Faradaic efficiencies of these hydrocarbons are largely dependent on, type and concentration of electrolytes, temperature, electrode potential, crystal surface, pH, and even the purity of the copper electrode.

Crystalline Cu electrode surfaces are known to increase the electrocatalytic activity in CO<sub>2</sub> electroreduction with the introduction of kinks and steps into atomically flat surfaces. Hori et al [15, 116, 117] were the first to study the electrochemical conversion of CO<sub>2</sub> in 0.1 M KHCO<sub>3</sub> aqueous solution, at many types of Cu single-crystal electrodes. They observed that crystal orientation of copper electrode greatly alters the reaction selectivity. C<sub>2</sub>H<sub>4</sub> was the important product with electrodes based on (100) terrace surfaces. The CH<sub>4</sub> formation was increased at Cu(111) or by the addition of (111) or (110) step atoms to the (100) basal plane. A Cu(S)-[n(111) x (111)] electrode gave large quantity of reaction products having more than two carbon atoms, while a (110) electrode derived from Cu(S)-[n(111) x (111)] specifically produced high yields of CH<sub>3</sub>CHO C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>COOH.

The catalytic activity of cuprous oxide (Cu<sub>2</sub>O) derived copper nano-particles on hydrocarbon selectivity in electrochemical CO<sub>2</sub> reduction has been studied recently [118]. Cu<sub>2</sub>O films with different crystal orientations and variable thickness were electrodeposited by reduction of Cu (II) lactate on Cu plates. During electrochemical CO<sub>2</sub> reduction by Cu<sub>2</sub>O structures, it was found that the selectivity of the process mainly depends on the thickness of parent Cu<sub>2</sub>O, rather than on the initial orientation of Cu<sub>2</sub>O crystal [118]. Besides CO and H<sub>2</sub>, selective production of C<sub>2</sub>H<sub>4</sub> was found with very high C<sub>2</sub>H<sub>4</sub>-to-CH<sub>4</sub> ratios (~8 to 12), while the thicker Cu<sub>2</sub>O films yielded a remarkably large amount of C<sub>2</sub>H<sub>6</sub>. Further, analysis of long term Faradaic efficiency of hydrocarbons indicated no sign of deterioration of the electrodes after 5 hours of continuous operation. Authors also observed the conversion of the Cu<sub>2</sub>O films in the presence of CO<sub>2</sub>, generating a nanoparticulate copper surface structure, before the formation of CO, hydrogen, and hydrocarbons using online mass spectroscopy and X-

ray diffraction data. This process may lead to selective production of industrially useful product  $C_2H_4$  with the optimization of surface area, size of the Cu nanoparticles, and number density as well as local pH of the surface.

Christina et al. [119, 120] reported oxide derived nanocrystalline copper catalyst prepared by annealing copper foil in air and electrochemically converting the resulting  $Cu_2O$  layers. They observed that the initial thickness of the  $Cu_2O$  layer strongly influence the  $CO_2$  electro-conversion activities of these electrodes. Thin  $Cu_2O$  films grown by annealing at  $130^\circ C$  resulted in catalysts whose activities were similar to those of polycrystalline copper. On the other hand,  $Cu_2O$  layers formed at  $500^\circ C$  with thickness  $\geq 3\mu m$  resulted in catalysts that showed high surface roughness that required 0.5 V less overpotential than polycrystalline copper to convert  $CO_2$  at a higher rate than  $H_2O$ . The combination of the above features gave  $CO_2$  reduction current densities  $>1\text{mA}/\text{cm}^2$  at overpotentials  $<0.4\text{ V}$  which implied better activity. The authors also reported that the activity of the modified electrodes was highly stable, in comparison to polycrystalline copper electrode under identical conditions. In another experiment, M. Le et al. (2011) [121] reported electro-reduction of  $CO_2$  to  $CH_3OH$  using several types of electro-catalysts including oxidized Cu electrodes. They studied the yield pattern of an electrodeposited  $Cu_2O$  film and explored relationships between reaction behavior and surface chemistry of air-oxidized and anodized copper catalyst.

Faradaic efficiencies (38%) and methanol yields ( $43\ \mu\text{mol cm}^{-2}h^{-1}$ ) obtained at  $Cu_2O$  cathodes were remarkably higher than anodized or air-oxidized copper cathodes suggesting Cu(I) species may play a major role in selectivity to methanol. Authors also showed methanol yields are dynamic and the Cu oxides are reduced to copper in a simultaneous process and indicated better stability of Cu(I) species could allow continuous methanol production.

### 3.3 Copper nanoparticles on Carbon nanospikes

Many catalysts [1, 120, 122-126] can convert  $CO_2$  to CO, but synthesis of liquid fuel requires that CO monoxide to be further reduced with  $H_2O$  as a  $H^+$  source. Further, though copper is the well known electrode with a significant CO electro-conversion activity, in bulk form its selectivity and efficiency for liquid fuel are very low for applications. Particularly,  $H_2O$  conversion to  $H_2$  is faster than CO conversion on copper catalyst unless very high overpotentials are used; in such cases gaseous hydrocarbons will be the main CO conversion products [52, 110]. Christina et al. (2014) [120] also showed that, crystalline copper derived from  $Cu_2O$  or 'oxide-derived copper' produces multi-carboxygenates such as acetate, ethanol, and n-propanol with Faraday

efficiency up to 57% at modest potentials in alkaline  $H_2O$  saturated with CO. The selectivity for oxygenates, with  $C_2H_5OH$  as the main product, shows the feasibility of a two-step reduction of  $CO_2$  to hydrocarbons.

In electrolytic cell for the reduction of  $CO_2$ , copper foil catalyst forms a mix of reaction products in aqueous solutions saturated with  $CO_2$ , which are dominated by (i)  $H_2$  at low overpotential, or (ii) CO and  $HCOO^-$  at high over-potential, or (iii) multi-carbon oxygenates and other hydrocarbons at the very high potentials [18, 22, 34]. Theoretical studies have predicted that Cu nanoparticles supported on graphene could increase electro-catalytic activity because of the strong copper-graphene interaction at defect sites [24] which in turn could stabilize the intermediates from  $CO_2$  electro-conversion and improve the selectivity of hydrocarbons such as  $CH_4$  and  $CH_3OH$  at lower overpotential. Studies have also shown, that the catalyst surface gets strongly influenced by adsorbed CO during the  $CO_2$  electroconversion; also CO acts as an intermediate in the generation of hydrocarbons [12, 51]. Y. Song et al (2016) have reported [34] a nano-structured catalyst for the electrochemical reduction of  $CO_2$  to  $C_2H_5OH$  with high Faradaic efficiency (63% at -1.2 V vs RHE) and high selectivity (84%) that operates at ambient pressure and temperature. The catalyst they developed comprises of copper nanoparticles as catalysts deposited on a highly textured film of N-doped carbon nanospikes. With DFT studies and electro-chemical analysis they have suggested a mechanism in which active sites on the copper nanoparticles and the carbon nanospikes work together to control the electrochemical conversion of CO dimer to  $CH_3CH_2OH$ . The high selectivity for this 12-electron reaction indicates that copper catalyst surfaces with nano-structures and multiple reactive sites in close proximity can yield novel reaction mechanisms. These are the best reported results so far in the electroreduction of  $CO_2$  into ethanol.

### 3.4 Catalyst stability and activity degradation

An understanding of the factors affecting the long-term stability of electro-catalysts is of increasing importance for the development of stable and efficient electro-catalysts as electrode materials for electroreduction of  $CO_2$  with high selectivity and Faradaic efficiency. While activity of catalyst is assessed by considering the onset potential for conversion as well as the Faradaic efficiency, catalyst durability is evaluated as per the changes in the behavior of catalyst with electrolysis time [102]. The production of poisonous intermediates and the deposition of inactive reactants on surfaces of electrodes are reported to be the main causes for catalyst deactivation [112, 127-131]. Several possible factors for catalyst deactivation as summarized by Hori et al. [129] are: (a) heavy metal impurities present in chemical reagents and subsequently added into the electrolyte solution;

(b) small quantity of organic molecules possibly contained in H<sub>2</sub>O, and (c) intermediate species/products generated during CO<sub>2</sub> conversion and adsorbed as poisons on electrodes. In addition to these, catalyst stability can also be affected by electrolysis condition and mode [119, 121, 132-134].

Further, Wu et al. [135] have observed that for pure Tin catalyst, a drop in performance could be caused by many factors: (a) cathodic degradation of the catalyst electrode surface [136], (b) deposition of non-catalytic species on catalyst surface (c) deposition of non-catalytic impurities from the electrolyte [135], and (d) anodic degradation at sites where gas bubbles are generated, which prevents cathodic polarization of the catalyst. For example, experiments conducted by Bujno et al. [137] showed that in diluted solutions Ni(I) complex catalysts present at the surface of electrode were converted into a Ni(0) carbonyl deposit which is catalytically inactive and hence, blocks the electrode surface against further catalysis. In another experiment, Benson and Kubiak [138] studied the deactivation pathway of the Lehn catalyst and indicated that it is due to the production of thermodynamically stable and catalytically inactive dimers [139-141]. Pugh et al. (1987) [142] observed that the electro-catalytic activity of cis-[Ru(bpy)<sub>2</sub>(CO)H]<sup>+</sup> gradually decreased over a prolonged period. Active species/sites on catalyst surface are responsible for the catalytic activity and hence are indispensable for electro-catalytic CO<sub>2</sub> conversion [119, 140, 143, 144]. Hence, loss in activity of catalyst is linked with the loss of active sites. One example is Ru-based complex catalysts slowly lose their carbonyl-containing complexes, due to the formation of inactive species such as [Ru(bpy)<sub>2</sub>(CO<sub>3</sub>)] during CO<sub>2</sub> reduction.

In order to improve the activity and stability of the catalyst, two major factors need to be considered: (1) the effect of type of catalyst, its composition and structure, and (2) operating conditions of the catalyst. An example of this phenomenon is Cu cathode deactivation after 3 hours of electrolysis at constant potential, while the activity of Cu catalyst remained stable for longer periods under superimposed potential method [145]. J. Lee et al. (2001) [145] observed the adsorption of amorphous carbon during cathodic conversion of CO<sub>2</sub> on Cu. After electrolysis for 60 minutes at constant cathodic potential, the amorphous carbon cathode poisoning resulted in the reduction of faradaic efficiency for the production of hydrocarbons such as C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub>. A change of the copper surface structure occurred with the production of Cu<sub>2</sub>O, when the potential modulation method was used. This structural modification inhibited the amorphous graphite adsorption leading to the constant

formation rate of CH<sub>4</sub> for periods as long as 7 hours of electrolysis. Another technique used is pulse electrolysis mode, which was observed to have a mitigating effect on cathode deactivation [146].

In other words, varying the electrolytic conditions led to a significant suppression of deposition of poisoning species on a copper catalyst, which mitigated the degradation of the cathode. C. W. Li et al. [119] observed that Cu<sub>2</sub>O layers formed by annealing copper foil in air at 500°C (thickness  $\geq 3\mu$  m) resulted in electrodes that showed large surface roughness and needed 0.5V less overpotential than polycrystalline copper to convert CO<sub>2</sub> at a higher rate than H<sub>2</sub>O. Equally important, the activity of modified electrodes was stable over a period of several hours; on the other hand, a polycrystalline copper electrode showed deactivation within 60 minutes under similar conditions. In another experiment, L. Wang et al. [147] reported that (110) oriented electrodeposited copper oxide films were found stable in a very narrow pH range,  $\sim 9.4$  to  $\sim 9.9$ .

## 4 Electrochemical cell for electro-conversion of CO<sub>2</sub>

The major limitations currently in CO<sub>2</sub> electroconversion to generate useful fuels, are: (i) rapid degradation of catalyst and (ii) slow transfer of CO<sub>2</sub> to the surface of electro catalyst. Both of these limitations are somewhat related to the design of electrochemical cell. While it has been shown that degradation of catalyst is primarily related to the catalyst material, the operating environment of electrolytic cell also plays a significant role. Thus, while improving the stability of catalyst, it is also important to look into innovative reactor designs to optimize the operating conditions which will result in better performance and long term stability. Some innovative designs for membrane-based electrochemical cells having gas diffusion electrodes (GDEs) developed in recent years appear to be the better approaches for decreasing internal resistance and improving the reactant mass transfer process.

In general, as mentioned above, the operating environment of the reactor is important for higher performance and stable operation of the electro-chemical cell. For example, a decrease in the temperature and an increase in the pressure lead to higher reaction rates due to an increased CO<sub>2</sub> concentration in the electrolyte.

While 0.5M KHCO<sub>3</sub> is a widely used electrolyte, the use of nonaqueous solutions improve CO<sub>2</sub> solubility and decreases the hydrogen evolution reaction [43]. Reaction products during CO<sub>2</sub> reduction depend upon a variety of factors such

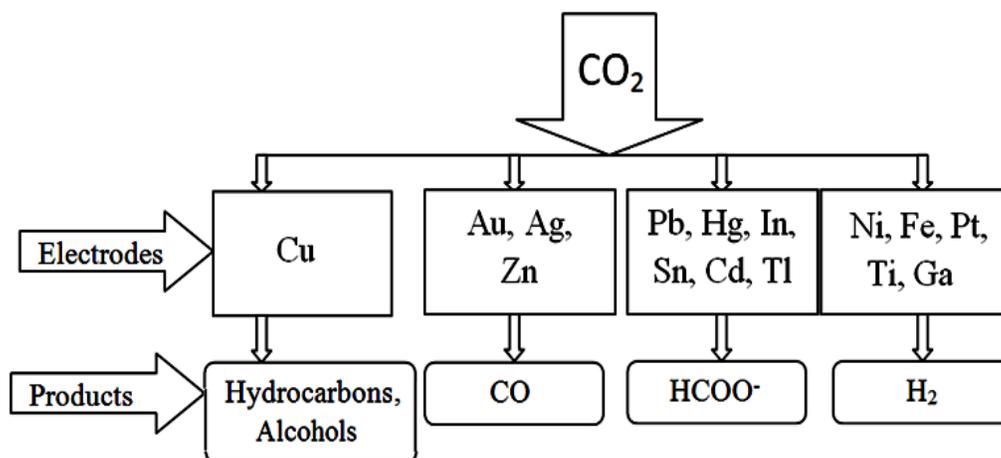


Figure 2: Main reaction products of CO<sub>2</sub> reduction on various catalysts.

as i) electrode/catalyst material, ii) Electrolyte including pH and iii) applied potential. However, based on the main reaction products they generate, electro catalysts can broadly be classified as shown in Figure 2 [13,148].

In the first group metallic copper is the only member which shows exceptional activity and selectivity for CO<sub>2</sub> conversion to hydrocarbons and alcohols. Au, Ag and Zn, in the second group release CO as the major product. The third group, consisting of In, Pb, Hg, Tl, Sn and Cd, produces formate as the major product; finally, hydrogen evolution is mainly observed in Ni, Fe, Pt, Ga, and Ti cathodes. It is interesting to note that CO is strongly adsorbed on electrodes of the fourth group; it is believed that the adsorbed CO blocks further conversion of CO<sub>2</sub>, giving rise in hydrogen evolution [148].

The above discussion refers to the structurally simple electrodes such as pure copper strip which is polished with fine emery paper and subsequently electro-polished in 85% phosphoric acid [13]. Electropolishing is generally used to smoothen the surface and remove irregularities after the mechanical polishing. Recent studies however, have highlighted the influence of the electrode surface structure and the method of preparation. Single crystal electrodes studies have shown that selectivity and activity in electrocatalytic CO<sub>2</sub> reduction depends on surface structure. Further, it has been shown that the single crystal copper electrodes with Cu(100) faces favor C<sub>2</sub>H<sub>4</sub> formation, while those with Cu(111) faces show increased selectivity for CH<sub>4</sub> [117]. Cu(110) faces show better yields for alcohols and non-gaseous C<sub>2</sub> and C<sub>3</sub> products in comparison with others.

Figure 3 shows a typical electrochemical cell for CO<sub>2</sub> electro-reduction. The electrochemical cell has a 3 electrode configuration. The working electrode, the cathode, located at a small distance from saturated Ag/AgCl electrode serving as reference electrode to reduce the electrolyte resistance. A Pt wire is used to make electrical contact with the cathode.

The Pt counter-electrode immersed in the electrolyte serves as an anode. A potentiostat and source meter are used to provide a constant bias/current between the electrodes. The anode and cathode compartments are physically separated by a proton-conducting membrane such as Nafion<sup>®</sup> 117. The electrolyte solution typically used is aqueous solution 0.5 M KHCO<sub>3</sub> both in anode and cathode compartments for CO<sub>2</sub> reduction. A continuous flow of pure CO<sub>2</sub> is introduced into the cell for saturating the electrolyte solution. This blocks interference from gas bubbles which strike the surface of electrode in the cathode compartment. The liquid products can be determined by sampling the liquid in the cell and analyzing the composition of the solution by NMR Spectroscopy; The gaseous reduction products can be analyzed using Gas-chromatography.

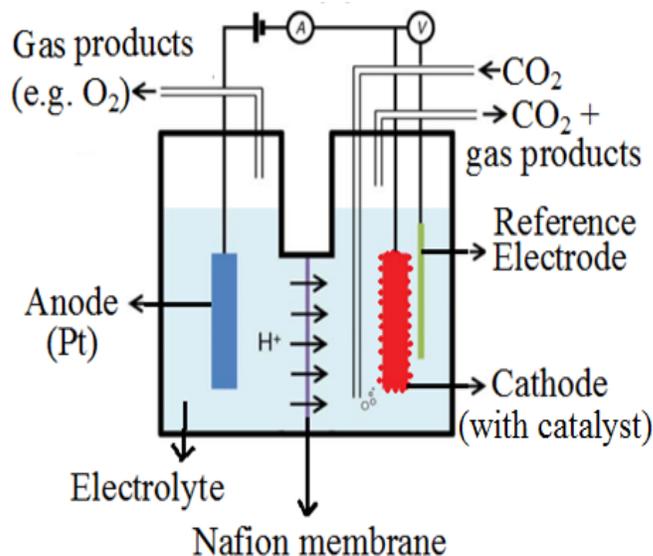


Figure 3: Schematic diagram of an electrolytic cell for electro-catalytic tests of CO<sub>2</sub> reduction in liquid phase.

## 5 Technological challenges in CO<sub>2</sub> electrocatalytic reduction into useful products

Technological challenges in CO<sub>2</sub> electrocatalytic reduction into useful products are many, primarily due to: low product selectivity, low catalyst activity, optimization of electrolyte electrochemical cell design and insufficient catalyst stability. Hence, current technology is still far from adequate for practical applications of CO<sub>2</sub> conversion to generate useful fuels. Hence, development of highly selective, active, and stable electro-catalysts for the electro-conversion of CO<sub>2</sub> is a major challenge. As described earlier in this review, for most of the catalysts developed so far, the overpotential for CO<sub>2</sub> electroconversion is rather too high, thereby suggesting that the activities of these catalysts are still not acceptable for large scale practical applications. Regarding low product selectivity, only some catalysts discussed above have resulted in better product selectivities and relatively stable yields under continuous operation. For example, the use of oxygen derived copper as well as nanoparticles on carbon nano-spikes have given best selectivities to date for the generation of ethanol and methanol [32, 34, 121]. The single biggest challenge currently in CO<sub>2</sub> reduction is insufficient catalyst stability or durability. While there are reports in the literature on stability tests upto 100 hours, there are no reports on long term tests. Among the problems regarding stability of catalysts, generation of carbon films and poisonous species (reaction intermediates) on the electrode surface, which lead to poisoning and blocking of the active sites on the surface of the catalyst is important. This leads to catalytic degradation as a reaction process. Among the other challenges of electro-conversion of CO<sub>2</sub> are optimization of electrodes and optimization of electrolytic cell.

The final challenge is the insufficient fundamental understanding of the CO<sub>2</sub> reduction process, especially with regard to catalytic selectivity and activity. Hence, a great deal of work needs to be carried out not only via experiments but also by theoretical modeling of activity and selectivity of catalysts.

This review gives an overview of development over several decades as well as recent results in the catalysis of CO<sub>2</sub> electroconversion. Various electro-catalysts are discussed and classified into metals, its complexes, and conducting polymers. The composition of electro-catalysts, conditions of reaction such as electrolyte, concentration, current or Faradaic efficiency, electrolysis potential, mechanisms of CO<sub>2</sub> electroconversion, and product selectivity are reviewed in detail. In general, almost all the pure metals including their composites which show some catalytic activity for CO<sub>2</sub> electroconversion have been studied for their electro-catalytic activity. Some progress has been realized during the past few

years in terms of product selectivity, catalytic activity, and catalyst stability. However, technology has still not advanced to a stage to enable the use of electro-catalysts for practical applications of CO<sub>2</sub> electro-reduction. Hence, breakthroughs in electro-catalysis are essential.

In the development of new catalysts, effort will have to be directed towards synthesis of new catalyst materials with new structures to realise novel catalysts with better performance. Two important catalyst materials are: (i) nano-structured catalyst materials, and (ii) composite catalysts, which can be synthesized by combining many different materials together. Optimized composite catalyst materials could have different catalytic performance than their individual components achieved with optimization of particle size, porosity, specific catalyst surface area, and active sites. Optimized catalysts should prevent agglomeration of particles and facilitate proton and electron conduction, and protect active materials from mechanical and chemical degradation.

## 6 Summary

The catalyst materials with nano-structure, such as nanoparticles, nanotubes/rods, nanoplates/sheet and others have unique properties, like high surface area and hence, can provide easy diffusion / transport pathways, leading to more efficient connectivity with electrolyte ions, faster kinetics, and better active sites for the electrocatalytic process. Further, the nano-structured materials can also be used as catalyst supports, such as copper nanoparticles on carbon nanospikes [34] for CO<sub>2</sub> electroreduction. In the present state of technology for CO<sub>2</sub> electroconversion to produce hydrocarbon fuels, the main limitations are slow CO<sub>2</sub> transfer to the cathode surface and rapid catalyst degradation, both of which are partially related to reactor design and the electrode. While catalyst degradation is primarily related to the cathode material, the operating environment of the cell also makes a significant contribution. Hence, improving reactor design and the electrode, to optimize the operating conditions of the cell for enhancing catalyst performance and catalyst stability is important. Nevertheless, significant progress has been made in certain novel designs for gas diffusion electrodes and electrolyte membrane-based electrochemical cells developed recently which help in improving the reactant mass transfer process and reducing internal resistance.

In summary, electroreduction of CO<sub>2</sub> to generate hydrocarbon fuels is a vital research and development area for reducing environmentally harmful CO<sub>2</sub>. Despite the many advances, the process of CO<sub>2</sub> electroreduction remains still challenging mainly because of the poor solubility of CO<sub>2</sub> in water at ambient pressure and temperature, the high over potential required, the poisoning of electrodes by reaction intermediates and expensive separation techniques

of byproducts. It is strongly believed that with focused and continued efforts on development of novel composite and nano-structured electrode materials to solve the challenges of low product selectivity, and catalytic activity, and also catalytic stability, the technology of CO<sub>2</sub> electroconversion would become practical in the foreseeable future.

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