



Electrochemical reduction of CO₂ for synthesis of green fuel

Karan Malik, Surya Singh, Suddhasatwa Basu and Anil Verma*

The depletion of increasing CO₂ of the atmosphere and the generation of alternate fuel sources are among the biggest challenges being faced by the scientific community across the globe. This scenario has propelled work in the direction of utilization of CO₂ by various methods. Electrochemical reduction of CO₂ is one of the leading research areas that may be useful not only for the utilization of CO₂ but also for the generation of green fuels and storage of renewable energy (solar or wind). However, the process is kinetically impeded and less selective toward a specific product and, therefore, requires efficient electrocatalysts. Much work has already been done in this field, and significant success has also been achieved. Hence, in this review paper, the potential of electrochemical reduction of CO₂ for fuel generation is discussed, with special focus on electrocatalysts. The suitability of different electrocatalysts is addressed along with the possible scope for enhancing the efficiency of the process. © 2017 John Wiley & Sons, Ltd

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INTRODUCTION

Energy requirements are continuously increasing and putting a lot of pressure on finite conventional energy resources. According to the projections of International Energy Outlook, natural gas, coal, and oil will be used for more than three-fourths of the total world energy consumption by 2040.¹ Since fossil fuels are limited as well as responsible for environmental issues, alternate sources need to be explored for sustainable energy supply. As per the recent report of the Intergovernmental Panel on Climate Change (IPCC), fossil fuels should be phased out completely in power generation by 2100 to keep their negative environmental impacts in check.² The increased use of fossil fuels has resulted in a higher CO₂ concentration in the atmosphere, which has crossed the level of 400 ppm.^{3–5} On the other hand, natural sinks for CO₂ sequestration, such as forest cover, are depleting. According to World Resources Institute, ~80% of the earth's forest cover has already vanished due to

deforestation in past century.⁶ It shows that natural CO₂ absorbers are being deteriorated at a fast rate, resulting in the increased carbon balance in the atmosphere. The widening gap between emitted CO₂ and sequestered CO₂ is an indicator that the existing sink needs to be assisted by some kind of artificial process that can perform the same function as the trees/forests. Therefore, scientists are trying to develop such processes that can not only fulfill the rising energy demands by the production of fuels but, at the same time, can also help in minimizing the excess CO₂ of the atmosphere. In this aspect, the electrochemical reduction of CO₂ (ERC) has become one of the most promising methods, which may convert CO₂ using renewable energy (solar or wind) to value-added chemicals that can serve the purpose of fuels. It has been conceptualized and accepted that plant functions can actually be mimicked using ERC.⁷

Green Fuels using Electrochemical Reduction of CO₂—Potential and Technical Aspects

The electrical energy (EE), preferably generated from renewable energy sources such as solar or wind, is supplied to an electrochemical reactor to carry out

*Correspondence to: anilverma@iitd.ac.in

Department of Chemical Engineering, IIT Delhi, New Delhi, India

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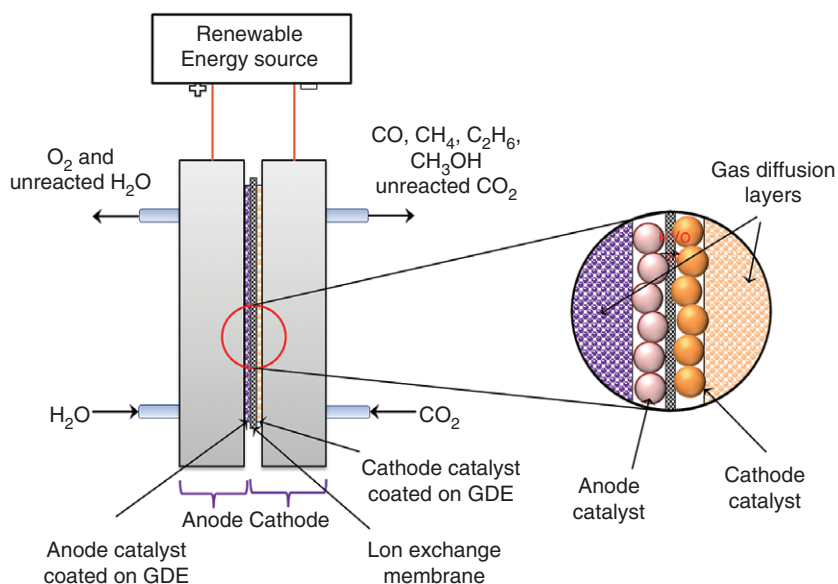
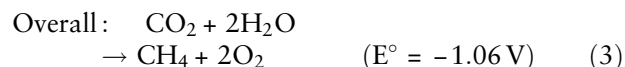
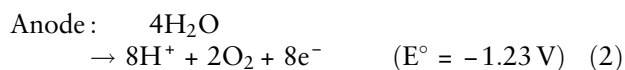
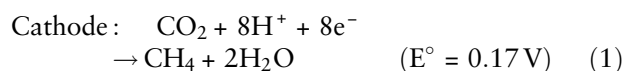


FIGURE 1 | Schematic of electrochemical reduction of CO₂ to various products.

ERC as shown in Figure 1. In the electrochemical reactor, CO₂ can be supplied directly in the gas phase or after solubilizing in an aqueous/nonaqueous medium. The former is termed as direct electrochemical reduction of gaseous CO₂ (dERC)^{8–14} and has higher practical applicability. ERC takes place at the cathode, resulting in the formation of value-added products (Eq. 1). Moreover, O₂ is produced at the anode by the electrochemical oxidation of H₂O as shown in Eq. (2). The overall reaction (Eq. 3) is shown for the formation of CH₄ as a representative reaction product. The equations show the corresponding standard potential (E°) of the reaction with respect to the standard hydrogen electrode (SHE).



ERC can result in a variety of products ranging from CO and hydrocarbons (HCs) to alcohols and acids, wherein the applied potential, electrolyte medium, and electrocatalysts play a decisive role.^{15,16} However, in this review paper, the discussion is focused on products that have high energy density, which may serve as ‘green fuel.’ Table 1 shows the overall reactions for the generation of such fuels with

TABLE 1 | Overall Reaction for the Formation of Various Green Fuels

Overall Reaction	E° (V)	EE (MJ/kg)
2CO ₂ + H ₂ O → 2CO + O ₂ + H ₂ O	−1.33	9.19
CO ₂ + 2H ₂ O → CH ₄ + 2O ₂	−1.06	51.15
CO ₂ + 2H ₂ O → CH ₃ OH + 1.5O ₂	−1.20	21.71
2CO ₂ + 3H ₂ O → C ₂ H ₅ OH + 3O ₂	−1.14	28.70
3CO ₂ + 4H ₂ O → C ₃ H ₇ OH + 4.5O ₂	−1.02	29.53

their corresponding standard electrode potentials (E°) and thermodynamic requirement of EE, calculated on the basis of Gibb’s free energy.

Figure 2 shows that the energy density of these green fuels is comparable with conventional fuels. It may be noted that HCs and alcohols can alone be used as fuel, whereas CO can be used as fuel in the form of synthesis gas (syn-gas) along with H₂, which is a by-product of ERC. Thus, as a method of producing alternate source of energy with an added advantage of mitigating CO₂, the potential of ERC seems to be viable and attractive.^{7,17,18} The research in the field of ERC is continuously growing, and many excellent reviews are also published covering various aspects, such as type of reactor, electrocatalysts, electrolytes, energy efficiency etc.^{15,18–26} However, even with multiple benefits, the process faces enormous challenges, which are mainly due to the stable nature of the CO₂ molecule, concurrent reactions, low product selectivity, mass transfer limitations, and fast deactivation of electrocatalysts.

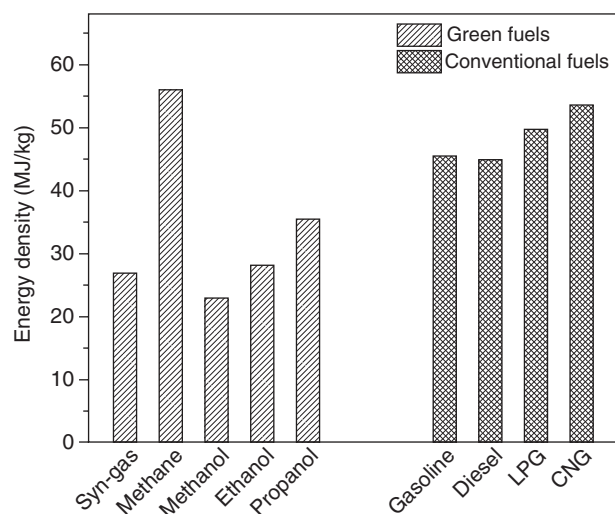


FIGURE 2 | Comparison of green fuel energy density with conventional fuels.

CHALLENGES IN ELECTROCHEMICAL REDUCTION OF CO₂ AND ROLE OF ELECTROCATALYSTS

In ERC, the first step is the activation of a stable CO₂ molecule. The carbon atom has double covalent bonds with the oxygen atom, and the two pairs of electrons are shared between the atoms. The electronegativity of carbon is much less than oxygen^{27,28}; still, CO₂ is a linear molecule because there are only two electron pairs on the central carbon atom, which are equally shared by two oxygen atoms on both the sides. Due to the linear *sp* hybridized structure, the bond strength of CO₂ is very high (~532 kJ · mol⁻¹²⁹), thus making it remarkably stable. Therefore, CO₂ needs substantial electrical potential in an electrochemical environment to be activated. The activation of CO₂ requires change in its geometry from linear CO₂ to bent CO₂ anion radical ($\bullet\text{CO}_2^-$), which results in a very slow self-exchange rate for the CO₂/ $\bullet\text{CO}_2^-$ couple, thus making this step rate determining.^{21,30} This is the most energy-intensive step in the ERC, and it theoretically requires -1.9 V versus SHE. Therefore, efficient electrocatalysts are required to reduce the activation energy barrier. Another issue is the simultaneous hydrogen evolution reaction (HER) at the cathode due to the close standard reduction potentials of CO₂ and H₂. Since H⁺ ions are indispensable for the formation of HCs and alcohols, its use in ERC is unavoidable. Thus, competition takes place between CO₂ electroreduction and HER at the cathode during ERC, which results in a significant consumption of supplied energy for HER instead of being used for ERC. Hence, current

efficiency of the CO₂ electroreduction process is adversely affected. Thus, electrocatalysts that can selectively catalyze the reduction of CO₂ are required. In view of this, the issue of electrocatalysts seeks the most attention among all other challenges. Moreover, in gas phase ERC, the challenge to increase the mass transfer is addressed by using a gas diffusion electrode (GDE), which increases the CO₂ concentration on the reduction site, whereas in case of aqueous phase ERC, the mass transfer limitation prevails due to very low solubility of CO₂ in water.

As per the literature reported till date, the electrocatalysts for CO₂ electroreduction can be broadly categorized into metals, metal oxides, and transition metal complexes. In few cases, metal hydrides and metal carbides have also been investigated. Many pure metals have been tested for ERC, but the problems of fast deactivation and low efficiency have led to the investigation of other substitutes. Deactivation in ERC may be either observed by a decrease in current density or an increase in the HER at constant current density. The decrease in current density is mainly due to the permanent surface coverage by the adsorption of foreign species (impurities) or reaction intermediates. Although the exact reason for increased HER at constant current density is still not known, some studies proposed that long-term ERC may produce some structural changes due to which ERC active sites become more active for HER.³¹ Metal oxides have always been found to be quite interesting, the reason being the soft acidic nature of the CO₂ molecule. This fact depicts that the presence of strong basicity phases such as oxides can enhance the CO₂ adsorption capacity of the catalytic surface,³²⁻³⁴ which will eventually enhance CO₂ reduction. The most attractive aspect of the use of metals and metal oxides is their ability to form HCs and alcohols. However, metal complexes are mostly selective toward CO formation, which needs two electron reduction of CO₂. For multielectron transfer products (viz. HCs and alcohols—Table 1), CO₂ requires some sort of stabilization of the metal-carbon (M-C) bond and/or ability of the electrocatalyst to accommodate multiple electrons so that the rate of electroreduction is much greater than M-C bond dissociation. Nevertheless, metal complexes are well known for lowering the activation energy barrier for the first electron transfer process as they allow their reasonable optimization due to the well-designed adaptations of either ligand or the central metal atom. Hence, for fuel quality products, most of the literature discusses the metals, metal oxides, and metal complexes. This review critically focuses on the selectivity and efficiency of various electrocatalysts

employed for ERC till date along with the possible areas for future investigations in this field. Moreover, Table 2 compiles the research of the past 10 years for the formation of fuel-type products using metals, metal oxides, and metal complexes.

ELECTROCATALYSTS FOR SYNTHESIS OF GREEN FUELS

Metal Electrocatalysts

A number of metal electrocatalysts are investigated for ERC to form potential green fuels. Therefore, these metal electrocatalysts have been reviewed with reference to the fuels and discussed in the following subsections.

Metals for CO Synthesis

CO is considered fuel because it can be used as syn-gas when mixed with H₂. Noble metals like Ag and Au serve as efficient electrocatalysts for CO formation from CO₂^{67–71} with Faradaic efficiency as high as 61–90% for Ag and 81–93% for Au at potentials –1.45 and –1.14 V versus SHE in aqueous solution, respectively.⁶⁹ The excellent performance by Ag for CO formation is also reported in ionic liquids as BMImCl (1-Butyl-3-methylimidazolium chloride) with Faradaic efficiency exceeds 99%.³⁷ However, large-scale use of noble metals is not acceptable due to their high cost. It was reported that Cd-modified Cu electrodes enhanced the production of CO.⁷² CO formation started to increase, while HCs became suppressed with increase in the amount of deposited Cd on copper. The same group again reported the enhanced current efficiency of CO on Cd-modified Ni electrodes with a simultaneous decrease in H₂ generation to a great extent.⁷³ These results suggest that Cd helps to enhance selectivity toward CO production. However, considering its adverse environmental effects, the use of Cd may not be very attractive. Azuma et al. reported the production of CO on pure Ni electrodes with 21% Faradaic efficiency at 0°C.⁷⁴ CO formation was also found using a Pd metal electrocatalyst; however, the Faradaic efficiency was quite low (~12%).⁷⁴ Hoshi et al. performed ERC on Pt and Pt group metals, which led to the production of CO in an aqueous solution.^{75–78}

Hara et al. investigated ERC in a 0.1 M aqueous KHCO₃ medium at ambient temperature and high pressure (30 atm) considering the fact that high pressure enhances CO₂ solubility in aqueous media.^{67,68} It was found that the ERC to CO with high Faradaic efficiency can be achieved at elevated

pressures. Figure 3 shows the Faradaic efficiency of CO formation using different metal electrocatalysts, which in turn indicates the selectivity of the metals for CO generation at 30 atm pressure. It can be seen that Ag and Au were the most selective, followed by Rh, Zn, and Pd etc. On the other hand, metals like Pb, Ti, Ta, and W were found to be the least selective for CO formation.

Hori et al. also demonstrated CO selectivity over various metal electrodes in ambient conditions and reported the order as Au > Ag > Zn > Pd > Ga > Cd > Sn > In > Cu in aqueous media.⁷⁹ It is noticeable that Ag and Au proved to be the best candidates for CO formation in both the ambient and high pressure conditions. As far as other metals are concerned, it was found that the reduction of CO₂ to CO at the Zn electrode is not very consistent as Faradaic efficiency ranges from 3 to 63.3% at a potential of –1.56 V versus SHE in ambient conditions; however, the reason is unknown. Sn and In are very less selective for CO, having Faradaic efficiency of only 2.4–4.1% and 0.9–2.2%, respectively. Furthermore, CO is not a primary product in case of Cu, and Faradaic efficiency ranges from 1.5 to 3.1% at –1.4 V versus SHE in ambient conditions.⁶⁹ DiMeglio et al. reported the use of Bi as an efficient electrocatalyst for CO production in ionic liquid with Faradaic efficiency as high as 95% at –1.71 V versus SHE.³⁸ Bi is nontoxic and hence environment friendly despite being extremely cheap. Therefore, it might be a good replacement of Ag and Au for CO production. Recently, a few workers have reported appreciable efficiency and selectivity for CO formation using bimetallic electrocatalysts, such as Cu-Au and Cu-In.^{80–82} A more straightforward goal in CO production can be the development of such an electrocatalyst that can optimize CO and H₂ (by-product of ERC) generation in a way to be directly used as syn-gas.

Metals for HCs Synthesis

Hydrocarbons (especially methane) have always been the choice as fuels. Having an energy density of 56 MJ · kg^{–1}, methane is quite a suitable fuel from the environmental safety point of view due to its high energy density and low CO₂ emissions compared to other fossil fuels. Methane, as well as other HCs formation using ERC, was studied by many workers, and most of them reported the use of Cu as an electrocatalyst. Hori et al. have shown that copper electrocatalyzes CO₂ for the selective formation of CH₄ and other HCs.^{69,79,83–85} In this case, the Faradaic efficiency of hydrocarbon formation was reported to be up to 60% in a 0.1 M KHCO₃ electrolyte using

TABLE 2 | ERC Research in Past 10 Years: Electrocatalysts for the Formation of Fuel-Type Products

Cathode Electrocatalyst	Electrolyte	Experimental Parameters	Main Products (Faradaic Efficiency, %)	References
Metal electrocatalysts				
Cu mesocrystals	0.1 M KHCO ₃	0.99 V vs. RHE	CH ₄ (1.5), C ₂ H ₄ (27.2)	35
Cu nanocubes	0.1 M KHCO ₃	0.60 V vs. RHE	C ₂ H ₄	36
Ag	1-butyl-3-methylimidazolium chloride (BMImCl) + 20 wt% H ₂ O	25°C, 1 atm	CO (>99)	37
Bi/Glassy carbon (GC)	CH ₃ CN	25°C, 1 atm	CO (95)	38
Fe	0.5 M H ₂ SO ₄	25°C, 1 atm	CH ₄ , C ₂ H ₆ , C ₂ H ₅ OH	39
Cu mesh	KHCO ₃	25°C, 1 atm	CH ₄ (19.4), C ₂ H ₄ (18.7)	40
Cu	0.5 M KH ₂ PO ₄	25°C, 1 atm	CO (40), HCs (30)	41
Cu-Ni	KHCO ₃ in water + methanol (8:2)	-5°C	HCs (26), CO (4)	42
Zn	Methanol + NaOH + Cu particles	-30°C	CO (60), CH ₄ (12)	43
Ni	0.5 M KHCO ₃	25°C, 1 atm	CO (1.7)	44
Metal oxide electrocatalysts				
Cu ₂ O films	0.1 M KHCO ₃	-0.99 V vs. RHE, 25°C, 1 atm	C ₂ H ₄ (34–39), C ₂ H ₅ OH (9–16), CH ₄ (<1)	45
Gd ₂ O ₃ nanoparticles/GC	0.1 M TBAH/CH ₃ CN	25°C, 1 atm	CO	46
Ir _{0.8} Ru _{0.2} -oxide on flat Ti surface	0.4 M Britton Robinson buffer solution (pH 5.82)	4 and 22°C, 1 atm	C ₂ H ₅ OH (96 at 4°C and 85 at 22°C)	47
CuO nanoparticles	0.2 M KI	1.5 V vs. SHE	C ₂ H ₅ OH (35) C ₃ H ₇ OH (5)	48
Cu (core)/CuO (shell)	1 M KHCO ₃	25°C, 1 atm	CO (23), CH ₃ OH (1–3)	49
γ-Ti ₃ O ₅	-	1-2.5 V	CO (7)	50
ZnO decorated with Cu nanoclusters	0.1 M KHCO ₃	-1.203 V vs. SHE	CO (5.4), CH ₄ (1.8), C ₂ H ₄ (10), CH ₃ OH (2.8), C ₂ H ₅ OH (10)	51
Cu from thick Cu ₂ O films	0.5 M NaHCO ₃	Q ≥ -5 C · cm ⁻²	CO (45), C ₂ H ₄ (5), C ₂ H ₆ (10)	52
Surface-oxidized Cu	0.5 M KCl	25°C	C ₂ H ₆ (27)	53
Electrodeposited Cu ₂ O	KHCO ₃	25°C, pH = 7.6	CH ₃ OH (38)	54
Cu ₂ O/Zn disk	KOH/methanol	-30°C, pH = 7.5	CH ₄ (7.5), C ₂ H ₄ (6.8)	55
Cu plate/Cu ₂ O	KHCO ₃	25°C, 1 atm	C ₂ H ₄ (22)/C ₂ H ₄ (28)	56
Pt + RuO ₂ /TiO ₂	0.5 M NaHCO ₃	25°C, 1 atm	CH ₃ OH (60.5)	57
Metal complex electrocatalysts				
(Re(CO) ₃ {α,α'-Diimine-(4-piperidinyl-1,8-naphthalimide)Cl}) complex	0.1 M TBAPF ₆ with external H ⁺ sources (CH ₃ OH, CF ₃ CH ₂ OH)	25°C, 1 atm	CO (68–92)	58
Ni Salen complex	Nafion-117 cationic solid polymer electrolyte	25°C, 1 atm	CO (40.7), CH ₄ (16.6), C ₂ H ₄ (2.1), C ₂ H ₆ (16.3)	14
Multimetallic porphyrin and polyoxotungstate-modified electrodes	DMF	25°C, 1 atm	CO, CH ₃ OH	59
	1 M KOH	25°C	CO	60

(continued overleaf)

TABLE 2 | Continued

Cathode Electrocatalyst	Electrolyte	Experimental Parameters	Main Products (Faradaic Efficiency, %)	References
Ag modified with 3,5-diamino-1,2,4-triazole (DAT)				
Ni/Co-terpyridine complex	0.1 M TBAP in DMF-H ₂ O	25°C, 1 atm	CO (38–76)	61
Pyridinium (pyrH ⁺) ion	<i>N</i> -methyl pyridinium ion	25°C	CH ₃ OH (30)	62
<i>N</i> -based organometallic silver	1 M KOH	25°C, 1 atm	CO (85)	63
Bimetallic Pd complex	DMF	1.04 V vs. NHE	CO (80)	64
Carbene-supported copper (I) boryl	Deuterated benzene	25°C, 1 atm	CO	65
Dinuclear Ni complex	Acetonitrile	25°C, 1 atm	CO	66

ERC, electrochemical reduction of CO₂; HCs, hydrocarbons; RHE, reversible hydrogen electrode.

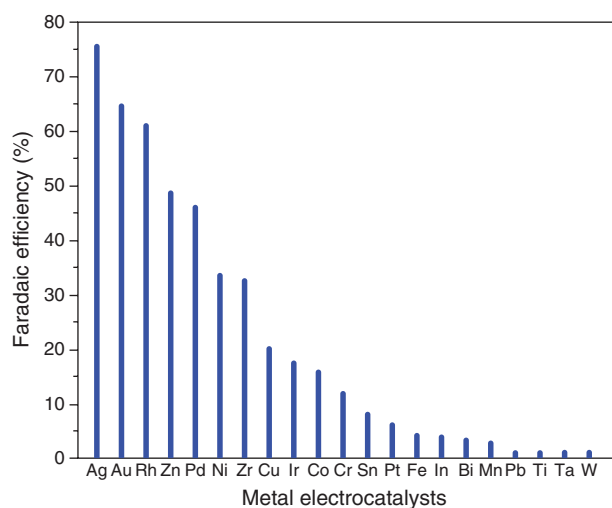


FIGURE 3 | Performance of metal electrocatalysts for CO formation in ERC at 30 atm pressure.

current density of $5 \text{ mA} \cdot \text{cm}^{-2}$ in ambient conditions.^{79,84} CO and alcohol formation were also found along with the HC as can be seen in Table 3. The electrocatalytic activity of Cu for hydrocarbon formation depends on several factors, such as temperature, pressure, type of electrodes etc. Hori et al. found the inverse relationship between Faradaic efficiency and temperature for methane formation over Cu, with Faradaic efficiency as high as 65% at 0°C while approaching 0% at 40°C.⁸³ In contrast to this, the formation of ethylene and CO was found to increase on raising the temperature as can be seen in the Table 3. The reason for the higher yield of methane at low temperature was reported due to the presence of longer lived intermediates. The effect of pressure on the activity of copper was also studied, and it was found that an increase in pressure opposes the hydrocarbon

formation.^{67,68} However, in this case, ethane was formed in trace amount, which was absent in ambient pressure conditions. The comparison of Faradaic efficiencies at ambient conditions and high pressure conditions shows that high pressure results in decreased HC generation but increased CO production (Table 3). Some researchers reported that the use of GDEs in place of foil electrodes increases the surface contact between the electrode/catalyst and CO₂, resulting in enhanced Faradaic efficiency.^{86–90} Therefore, the effect of GDE was also investigated over the activity of Cu, and in this case, the overall reduction of CO₂ was found to be increased over GDE in contrast to foil electrodes. The current density on the Cu-loaded GDE was found to be almost two orders of magnitude higher than that on the Cu foil electrode.⁸⁶ However, CH₄ formation over GDE was decreased as compared to foil electrodes (Table 3). Other workers showed that the applied potential can also change the selectivity and product distribution to a great extent.⁹¹ As the applied potential becomes more negative, the formation of HC takes place, while at less negative potentials, CO prevails. Moreover, surface properties of metals like roughness and purity are also important parameters for determining the methane formation as it affects the adsorption characteristics of the electrode. The smooth surface gets poisoned very soon, whereas a rough surface maintains the catalytic activity for a longer duration.⁹² Even the method of pretreatment of the electrode surface affects the product distribution over Cu to a great extent. While the untreated Cu results in increased CO formation with time, the electrolytically treated Cu remains stable with time and continues to produce HCs. On the other hand, the air-oxidized Cu electrode preferentially produces H₂ with very little CH₄ production.⁹³ In addition, the crystal structure

TABLE 3 | Faradaic Efficiency of Products at Different Conditions using Cu Electrocatalyst

Products	Faradaic Efficiency of Products on Cu Electrode (%)							
	Cu Foil ¹ 25°C, 1 atm	Cu foil ² Temperature Variable, 1 atm					Cu foil ³ 25°C, 30 atm	Cu GDE ⁴ 25°C, 1 atm
		0°C	10°C	20°C	30°C	40°C		
CO	2	0.4	1	2	5	7	20.1	40
CH ₄	29.4	65	58	50	16	5	9.95	12
C ₂ H ₆	–	–	–	–	–	–	0.06	–
C ₂ H ₄	30.1	2.5	7.5	10	15	20	3.74	18.2
Alcohols	9.9	–	–	–	–	–	–	5.4

¹ KHCO₃ solution (0.1 M) at –1.41 V vs. SHE.⁸⁴

² KHCO₃ solution (1 M) at –1.33 to –1.39 V vs. SHE.⁸³

³ KHCO₃ solution (0.1 M) at –1.44 V vs. SHE.⁶⁷

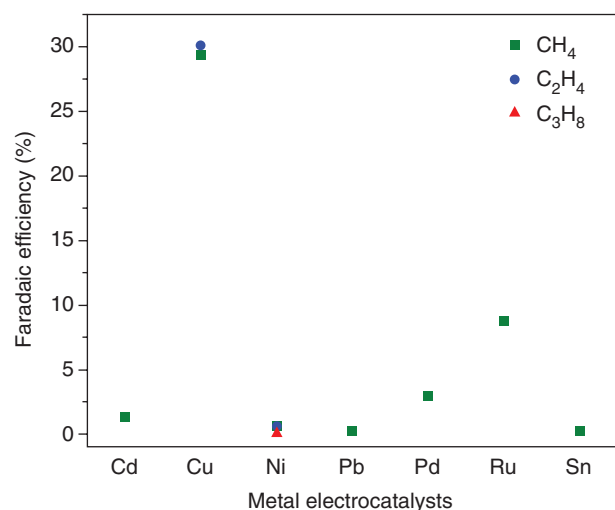
⁴ K₂SO₄ solution (0.5 M) at –1.25 V vs. SHE.⁸⁶

of the electrocatalyst plays an important role as the selectivity for an individual reaction may depend on the atomic configuration of the electrode surface. It was found that the rate of CH₄ formation in CO₂-saturated 0.5 M KHCO₃ is the highest in Cu (111), followed by Cu (110) and Cu (100).^{84,94}

Although Cu is the most widely used electrocatalyst for HC formation, the problem of deactivation of the copper electrode limits its continuous use in a reaction. Hori et al. investigated the deactivation of the Cu electrode and reported that the impurities (especially Fe⁺² and Zn⁺²) present in the electrolyte are the major contaminants.⁹⁵ It was suggested that these impurities can be removed by the pre-electrolysis of the electrolyte solution. However, this view is questioned by Ogura⁹⁶ because Yano et al.⁹⁷ showed that by increasing the concentration of electrolyte, the product formation (C₂H₄)

increases. Thus, the increased concentration of the (heavy) metal impurities due to increased electrolyte concentration indicates that the heavy metal impurity does not poison the Cu electrocatalyst. Other workers have pointed out that it is an adsorbate of unknown composition over the copper cathode that causes poisoning,^{98,99} and the deactivation caused by such an adsorbate can be overcome by pulse-mode electrolysis. Lee et al. also suggested that the cause of copper poisoning may be the adsorption of some species, such as graphite, originating from adsorbed CO (CO_{ad}) on the Cu surface, and in this case too, pulse modulation helps.¹⁰⁰

Frese et al. studied the CH₄ formation over the Ru electrode in an acidic medium using the 0.1 N H₂SO₄ electrolyte and found that the activity of Ru was affected by the pH, temperature, electrolyte purity etc.¹⁰¹ In this case, however, the current density was less, and electrode instability was also an issue. Kudo et al. reported the hydrocarbon formation over the Ni electrode using the 0.1 M KHCO₃ electrolyte in ambient as well as in high pressure (60 atm) conditions. They found that high pressure conditions enhance the formation of HC with decreased H₂ evolution.¹⁰² The same phenomena was also observed by Hara et al. using Pt-loaded GDEs at 30 atm pressure, where Faradaic efficiency for CH₄ formation reached up to 35% at a current density of 900 mA · cm⁻² (⁶⁸ Pt). A small amount of ethane and ethylene formation was also found. Over Pd and Cd electrodes with the 0.1 M KHCO₃ electrolyte, methane Faradaic efficiency was found to be 2.9 and 1.3%, respectively.⁷⁵ Sn and Pb electrodes also produced scanty amounts of methane with Faradaic efficiency of 0.2% for each³. Figure 4 shows the comparison of the Faradaic efficiencies of different metal electrocatalysts for hydrocarbon formation.^{69,75,83,101,102}

**FIGURE 4** | Faradaic efficiency of metal electrocatalysts for hydrocarbon formation.

Summarizing all these studies, it can be said that, as of now, Cu catalyzes ERC for HC formation efficiently. In order to design new electrocatalysts, investigations over bimetallic or core-shell electrocatalysts may be investigated, where the electronic perturbations caused by one metal to another can tune the efficient conversion of CO₂ into HCs. Recently, a few studies suggested that the adjustment of binding energies of the intermediate with the electrocatalyst may promote the formation of a particular product.^{80,81} Bimetallic systems are able to tune the binding energy of metals. The basic reason for the change in binding strength is the charge (electron) transfer in these bimetallic systems.¹⁰³ Therefore, it might help in the selective formation of HCs.

Metals for Alcohols Synthesis

CO₂ to CH₃OH conversion is also a promising approach because methanol can be used directly as a fuel and as a reactant in fuel cells. Frese et al. reported the use of electroplated Ru electrodes and achieved CH₃OH formation with Faradaic efficiency of 42% at 60°C at the potential of -0.31 V versus SHE in the 0.2 M Na₂SO₄ electrolyte.¹⁰¹ Summers et al. reported the production of CH₃OH with ~100% Faradaic efficiency over Mo electrodes in an acidic solution of Na₂SO₄.¹⁰⁴ However, it was found that the electrode becomes corroded but could be overcome up to a certain extent by cycling the

potential. Olah et al. reviewed the electrochemical production of methanol from CO₂ and suggested an increase in the efficiency of the process by the use of simultaneous H₂ production in ERC.¹⁰⁵ The system can be optimized in such a way to maintain the CO:H₂ ratio as 1:2. Furthermore, the (CO + H₂) can be directly converted to CH₃OH in the same electrochemical reactor. In this way, the applied energy may be used efficiently. Figure 5 shows the schematic of a conventional electrochemical pathway and Olah's pathway for CO₂ to CH₃OH formation. Kuhl et al. also reported the formation of higher alcohols using NMR spectroscopy over a metallic copper surface; however, the Faradaic efficiencies for ethanol, n-propanol, and allyl alcohol production were quite low (10, 4, and 1.7%, respectively).¹⁶ A few other workers also discussed the CH₃OH production over metal oxide surfaces. It can be said that alcohol formation using ERC still needs significant efforts. Although the possibility to synthesize higher alcohols using ERC is undoubtedly proven, suitable electrocatalysts are required for the selective and efficient conversion of CO₂. Lessons can be learnt from Olah's view,¹⁰⁶ and in spite of direct alcohol synthesis from CO₂, a syn-gas route may be preferred (Figure 5). In this respect, increased CO adsorption over a catalyst surface would be beneficial for alcohol formation, and to increase the yield, high surface area electrocatalysts may be utilized.

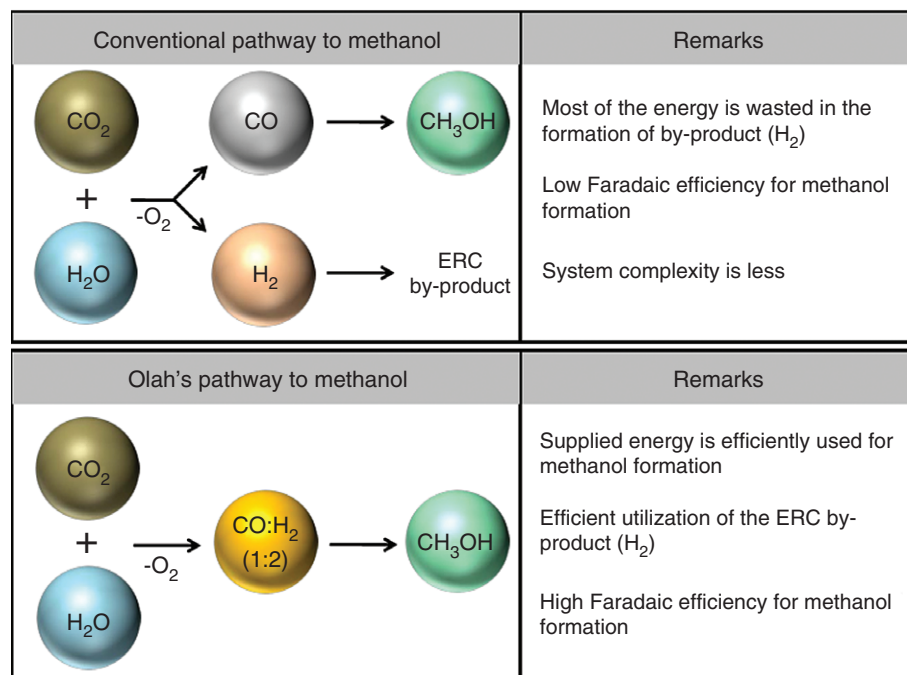


FIGURE 5 | Schematic of conventional and Olah's pathways for methanol formation using ERC.

Metal Oxide Electrocatalysts

The use of metal oxides in ERC is advocated considering the acidic (Lewis acid) nature of CO₂. Since metal oxides are basic in nature, their use as electrocatalysts can enhance the adsorption of CO₂, thereby increasing the efficiency of the process.^{52,107–110} Moreover, in ERC, the use of metal oxides was also intended to overcome the problem of metal deactivation (especially in case of copper) due to surface changes caused by oxide formation and to find the possibility of alcohol production as no specific metal electrocatalyst was found suitable for it.

As discussed earlier, copper is the metal over which the highest attention is paid due to its selectivity mainly toward HCs and, up to some extent, for alcohols formation too. Nevertheless, due to its fast deactivation in the reducing environment, continuous use was not possible. Therefore, it was suggested that a change in the surface structure might impart some stability to the pure metal. In view of this, many workers have tried cuprous oxide (Cu₂O) in place of metallic copper surfaces. It was reported that Cu₂O exhibits high Faradaic efficiency for CO₂ reduction at considerable low overpotential.^{53,54} The major benefit of Cu₂O is its resistivity toward deactivation due to surface changes caused by the oxidation of Cu, which does not allow for graphite adsorption.¹⁰⁰ It is also said that Cu₂O enables the easy formation of •CO₂⁻ intermediate and decreases H⁺ reduction,⁵² which allows Cu₂O to yield HCs for a longer duration without being much affected by poisoning.

Table 4 shows the comparison of widely used pure metal electrocatalysts with their corresponding metal oxides for the formation of ERC products. It can be seen in the table that Cu₂O shows higher overall Faradaic efficiency for ERC. The use of Cu₂O increases the CO and alcohol formation substantially as compared to the Cu electrocatalyst. CH₃OH production was also reported over Cu₂O surfaces by Le et al. with Faradaic efficiency as high as 38%.⁵⁴ Where Cu(0) electrodes favor the formation of only

HCs, it was proposed that Cu(I) species play a selective role toward methanol formation by offering more stability to intermediates and enabling the formation of H₃CO adsorbates.¹¹¹ This causes the next hydrogenation step to occur at the oxygen atom rather than the carbon atom, thus favoring the formation of methanol. It may be noted that the Faradaic efficiency for hydrocarbon formation reduced when a metal oxide was used.⁵² However, the exact cause of the higher activity of Cu₂O and its reduced tendency toward deactivation is not yet established. It can be hypothesized that, somehow, oxide surfaces reduce the competitive HER, which in turn results in increased activity toward CO₂ reduction. The Faradaic efficiency toward CO formation increases significantly for Cu₂O as compared to Cu (Table 4), which may be due to the formation of highly dispersed Cu nanoclusters as a result of the oxide reduction of the Cu surface over which CO formation prevails.¹¹² It is also reported that the HER prevails over oxophilic sites¹¹³; so, it might happen that Cu₂O provides lesser oxophilic sites than pure copper. This may provide an explanation for the better electrocatalytic activity of cuprous oxide surfaces than the pure Cu metal. Moreover, the changes introduced in terms of defects over the metal surface after oxide formation can also be a probable reason for the better activity toward ERC. Increased adsorption of CO₂ over oxide surfaces can also be a reason for increased efficiency in ERC. As shown in Figure 6, the metal oxides have a basic character due to the electropositive nature of the metals, while CO₂ is Lewis acid. Therefore, cations and anions of the metal oxide possess a partial positive and negative charge, having the tendency to adsorb (acidic) CO₂.¹¹⁴ Thus, most of the sites are occupied by CO₂, which in turn results in increased reduction.

Andrews et al. reported the production of HCs and alcohols using the Cu nanoclusters on single crystal (10 $\bar{1}$ 0) ZnO electrodes.⁵¹ The combination of Cu and ZnO produces CO, CH₄, C₂H₄, CH₃OH,

TABLE 4 | Comparison of Electrocatalytic Activity of Metals and Corresponding Metal Oxides

Products	Cu ¹		Cu ₂ O ²		Ru ³		RuO ₂ ⁴	
	E (V)	FE (%)	E (V)	FE (%)	E (V)	FE (%)	E (V)	FE (%)
CO	-1.41	2	-0.35	40	-0.31	1.2	-0.56	NR
HCS	-1.41	59.5	-0.95	15	-0.31	11	-0.56	NR
Alcohols	-1.41	9.9	-0.86	38	-0.31	42	-0.56	30.5

Note: (E, Potential (V vs. SHE); FE, Faradaic efficiency; NR, Not reported).

¹ KHCO₃ solution (0.1 M) at -1.41 V vs. SHE.⁸⁴

² NaHCO₃ solution (0.5 M) for CO and HCS⁵²; KHCO₃ solution (0.5 M) for alcohols.⁵⁴

³ Na₂SO₄ solution (0.2 M).¹⁰¹

⁴ NaHCO₃ solution (0.5 M).¹¹⁰

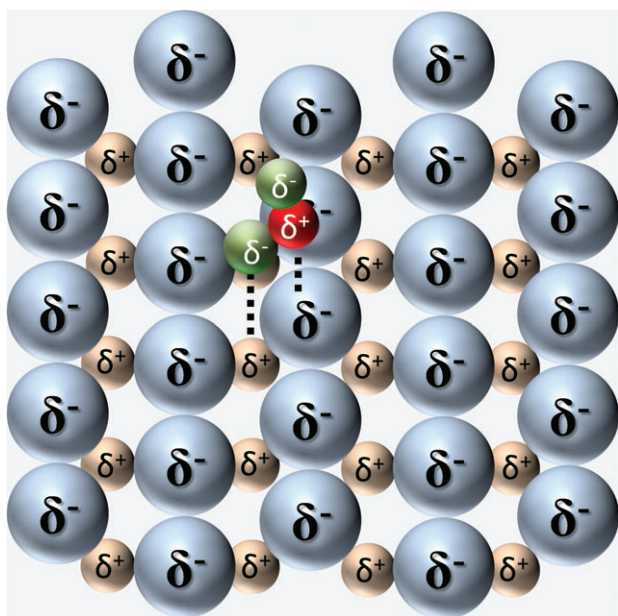


FIGURE 6 | Representation of the acidic and basic character of the CO_2 and metal oxide, respectively, which helps in adsorption of CO_2 over the electrocatalyst surface (red and green spheres represent C and O, respectively, while brown and blue represent the cations and anions of metal oxide electrocatalyst, respectively).

$\text{C}_2\text{H}_5\text{OH}$, and trace levels of $\text{C}_3\text{H}_7\text{OH}$. Similar Faradaic efficiencies of Cu/ZnO electrodes were found relative to Cu electrodes, with the exception of alcohols, where selectivity was improved. Metal oxide surfaces of Ru were also investigated for alcohol production. Many workers have carried out ERC using Ru and RuO_2 . However, Table 4 shows that the activity of RuO_2 as compared to Ru does not seem to be favorable. The performance of RuO_2 over Ru shows decreased Faradaic efficiency for alcohols (Table 4). The deactivation is not reported in this case, but high overpotential of RuO_2 , limits its use in place of Ru. Kumari et al. studied the CO_2 reduction on CeO_2 . A mechanistic route with the most favorable orientation and low binding energy of the intermediates, formate and carboxyl, for the formation of the CH_3OH was studied through the DFT calculations.¹¹⁵ They concluded that the carboxyl (intermediate) so formed reacts via a reverse water gas shift reaction mechanism and produces CO, which may be hydrogenated to produce methanol. However, formate (intermediate) is tightly bonded on the Ce surface and likely does not form methanol. Although the overall reaction was governed by the reaction kinetics, the extended CeO_2 surface also played a key role in the selective production of methanol.

Bandi reported the work over conductive metal oxides and use of surface adatoms in ERC.¹¹⁶ A

combination of various conductive metal oxides were used, and it was found that $\text{RuO}_2 + \text{TiO}_2$ (35 + 65 mol%) and $\text{RuO}_2 + \text{Co}_3\text{O}_4 + \text{SnO}_2 + \text{TiO}_2$ (20 + 10 + 8 + 62 mol%) show high current efficiencies for CH_3OH production in the solution of 0.2 M Na_2SO_4 (pH = 4) saturated with CO_2 . Later, reactions were carried out in CO_2 -saturated KHCO_3 solution at pH 4–7 over $\text{RuO}_2 + \text{TiO}_2$ electrodes, but only a small amount of CO_2 reduction could be achieved; however, when electrodeposited Cu was added over $\text{RuO}_2 + \text{TiO}_2$ electrodes, Faradaic efficiency of CH_3OH formation was increased to 30%.¹⁰⁷ Popic et al. also discussed the production of CH_3OH using surface adatoms.¹¹⁰ The Ru surface was modified by adding an adatom of Cu and Cd, and the reaction was carried out in 0.5 M NaHCO_3 at a potential of -0.56 V versus SHE, which resulted in the production of CH_3OH with efficiencies of 17, 41, and 38% after 480 min of electroreduction using RuO_2 , RuO_2/Cu and RuO_2/Cd electrodes, respectively. It was found that surface modification with a little amount of metals having high hydrogen overvoltage diminishes the HER, which in turn enhances the efficiency of CO_2 reduction. The surface structure of adatoms also plays an important role as shown by Qu et al. who reported the formation of CH_3OH over Pt electrodes modified by $\text{RuO}_2/\text{TiO}_2$ composite nanotubes and $\text{RuO}_2/\text{TiO}_2$ composite nanoparticles.⁵⁷ It was found that a Pt electrode modified by the $\text{RuO}_2/\text{TiO}_2$ nanotube composites resulted in a more efficient formation of CH_3OH (Faradaic efficiency 61%) compared to $\text{RuO}_2/\text{TiO}_2$ nanoparticle-based composites (Faradaic efficiency 40%) in NaHCO_3 solution, the reason for which is not enunciated.

Metal Complex Electrocatalysts

As stated earlier, metal complexes lower the activation energy barrier for the first electron transfer process due to their well-designed adaptations of either ligand or the central metal atom, and hence, efficiencies achieved in the case of metal complexes are quite high as compared to metals or metal oxides. A number of transition metal complexes have been reported to selectively favor CO formation.^{64,65,87,88,117–127} A stable CO_2 and a transition metal adduct was reported as $(\text{Co}(\text{salen})(\text{CO}_2)\text{M})^+$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Cs}$) by Gambaotta et al.¹²⁸ Phthalocyanin complexes of Co were also proven to be very active toward the ERC for CO generation.¹²⁹ The Co phthalocyanin complex is reduced easily, and thus, CO_2 transformation could be carried out at low overpotential values with faster rates. Hawecker et al. reported selective

and sustained CO production in a DMF:H₂O (9:1) solution using bipyridine ligands at low potential.¹³⁰ Tetra-aza-macrocyclic complexes of Co and Ni are interesting in the sense that the product ratio of CO/H₂ obtained was 1:1 or 2:1, which can be used as syn-gas after proper modulation.¹³¹ Simon-Manso et al. reported the use of dinuclear Ni complexes for the formation of CO.⁶⁶ Phosphine ligands are also very well reported for ERC, the first being the Rh(dppe)₂Cl (dppe = 1,2-bis(diphenylphosphino)ethane) complex reported in 1984 by Slater et al.¹³² However, it only resulted in the formation of formate, and no CO was observed. Later, phosphine ligands of Pd complex were studied, and it resulted in the formation of CO in acidic solutions. It is important to note here that the basicity/redox potential of the phosphine ligands is crucial for the formation of CO as more negative redox potential results in the formation of H₂.^{64,133,134}

Metal complexes do not seem to be very effective for hydrocarbon and alcohol formation possibly because the contact time of the CO₂ with the catalyst is limited, and the metal-carbon bond gets dissociated quickly; thus, the multielectron transfer mechanism gets hindered. However, some efforts were made, and HCs and alcohols production is reported in few of the cases.^{13,14,59,62,135–137} Furuya et al. and Magdesieva et al. reported the formation of CH₄ using Cu, Ga, and Ti phthalocyanins.^{135,136} Seshadri et al. reported the pyridinium ion for CH₃OH production as a novel homogeneous electrocatalyst with Faradaic efficiency of ~30%. Labeling studies with ¹³CO₂ were performed to verify the formation of ¹³CH₃OH.^{62,137} Garcia et al. studied the multimetallic porphyrins/polyoxotungstate-modified multilayer Indium tin oxide (ITO) electrodes for the ERC. It was found that the electrocatalytic activity is governed by the metal ion in the center of the porphyrin. Three different metal ions, viz. Mn(III), Ni(II), and Zn(II), were investigated. Formation of CO (3.85 × 10⁻² mM) was found when ITO was modified with the Ni(II) metal ion at the center of the porphyrin. However, the ITO electrode modified by Mn(III) and Zn(II) ions resulted in the formation of CH₃OH with 6.99 × 10⁻³ mM and 3.8 mM concentrations, respectively.⁵⁹ Recently, the salen ligand complex of Ni has been reported to achieve 74% of Faradaic efficiency for the reduction of gaseous CO₂ with the formation of HC (CH₄, C₂H₄, C₂H₆) as well as CO.^{13,14} In this case, the redox property of the metal complex was found to be responsible for the efficient reduction of CO₂.

Plenty of work is done with the metal complex electrocatalysts, and success is achieved for CO

formation, but hydrocarbon and alcohol production has to go a long way. Moreover, a detailed review on the application of metal complex electrocatalysts in ERC is provided by Benson et al. and Inglis et al.^{138,139}

Metal Carbides and Metal Hydrides Electrocatalysts

Metal carbides and metal hydrides are not well studied as compared to metals, metal oxides, and metal complexes. Carbides of group V elements (V, Nb, and Ta) have been investigated for their electrocatalytic activity in ERC by Yotsuhashi et al., and the production of CO, CH₄, C₂H₄, and C₂H₆ was reported at low overvoltages.¹⁴⁰ However, when carbides of metals other than group V (e.g., Mo, Ti) were tested, only hydrogen evolution could be observed, for which no plausible reason was given (^{13,14,140} (Protocol)). There is no other reported work over metal carbides to our knowledge.

Pugh et al. investigated the key steps in ERC for the insertion of CO₂ into an M-H bond. Studies were carried out for Ru bipyridine complex *cis*-(Ru(bpy)₂(CO)H)⁺, which acted as a catalyst for ERC and resulted in the formation of CO. Here, the insertion of CO₂ into the Ru-H bond is preceded by the bipyridinium-based reduction of *cis*-(Ru(bpy)₂(CO)H)⁺. The second step is the reformation of the M-H bond by the reduction of water.¹⁴¹ Late transition metal hydrides were also found to reduce CO₂, where trialkylboranes play a key role.¹⁴² It is thought that the chemistry involves assistance of trialkylborane, which forms a formate-borane adduct, thus favoring the CO₂ reduction; however, further investigations are still going on.

ERC—FUTURE GOALS

Although significant attempts have been made to develop suitable electrocatalysts in ERC for fuel production, a breakthrough is yet to come. Simultaneous HER is still the biggest issue to tackle as it renders low CO₂ conversion efficiency. Another major aspect that needs focus is the research on various causes of deactivation of cathodic electrocatalysts, which affect performance seriously. Furthermore, the information for predicting the activity of electrocatalysts in ERC is still lacking due to the complexity of the CO₂ electroreduction reaction and occurrence of other simultaneous reactions. Research to determine exchange current density,¹⁴³ volcano curve,^{144,145} turnover rates²¹ etc. is crucial for gathering in-depth knowledge of ERC. Density functional theory (DFT) may

also be employed for the design and modulation of the electrocatalyst.^{146,147} Apart from cathode electrocatalysts, research on anode electrocatalysts is also required. Appropriate performance of anodic electrocatalyst relative to cathode is needed for the efficient functioning of ERC. Replacement of noble metals with cheap and environment-friendly anodes is advocated. Investigations on selective electrolytes^{8–10} are also important as they play an important role in tuning the reaction zone, which ultimately affects the selectivity of the products. To make the process more practical, the use of solar energy is indispensable; however, proper synchronization of the performance of photo-anode and photo-cathode is the real challenge in this direction.^{17,24,148} As nanostructured and porous materials always play a paramount role in electrocatalysis, with the advancement in nanotechnology, solid state electrochemistry, and catalysis, the development of suitable photo-electrodes is expected.

SUMMARY

In this review, the electrochemical reduction of CO₂ was discussed for the synthesis of green fuels with special reference to the cathode electrocatalyst. Enough possibilities for CO, HC and alcohol product formation were found. It was seen that the metal oxides were less prone to poisoning as compared to the metal electrocatalysts. Hydrogen, an ERC by-product, may also be well utilized for the production of syn-gas. However, more research is required for increasing Faradaic efficiency of products formation. Furthermore, research in the field of CO₂ capture and renewable energy storage will also help to maximize the utilization of this process. In view of all these facts, it was found that besides having so many challenges, the electrochemical reduction of CO₂ has ample scope for improvement.

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