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Electro-catalytic and photo-catalytic reformation of CO₂— reactions and efficiencies processes (Review)

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Abstract. Energy harvesting with lowest environmental impact is one of key elements for cleaner future. Photocatalytic as well as electrocatalytic CO₂ reformation processes are considered as prominent methods. Thus, extensive research of CO₂ reformation is being done to find the right materials that holds crucial qualities. For photocatalysis that includes pronounced separation of light-generated opposite sign charge carriers, sensitivity to visible light, high quantum yield. In electrocatalysis high CO₂ adsorption, chemical stability, multielectron reaction catalysts are necessary. Additionally, materials participating in the reaction process must be provided with charge carriers at proper reduction and oxidation potentials. To meet the set goal of lowering environmental impact and lower CO₂ amounts exhausted into the atmosphere by human activities, it is necessary to find right technology for capturing, storing, and reusing carbon dioxide. Various technologies and materials in different levels of readiness are available and under development, such as CuO loaded TiO₂ nanotubes for photocatalytic reformation or electrocatalytic reduction on copper. Not only the proof of concept is necessary but estimation and more importantly determination of the efficiency of both electro and photo catalytic reformation of CO₂. In this work review of reactions and efficiency of both processes based on existing established technological methods is done.

1. Introduction

It is well known that proactive steps towards pollution reduction and shift from oil based energy are being pursued not only generally by legislation and agreements [1] but also by long term development strategy and research, such as EU climate-neutral plan by 2050. Not only energy harvesting with lowest environmental impact is one of key elements for cleaner future, but also use of accessible resources more efficiently. Electrocatalytic and photocatalytic CO₂ reformation are considered as prominent methods for lowering atmospheric pollution and providing possible shift to more sustainable energy production. CO₂ can be reformed into various hydrocarbons that can be directly used as fuel or substitute conventional chemical production. Extensive research on CO₂ reformation is being done to find the right materials for successful catalytic CO₂ reduction. It is known that straightforward CO₂ reduction requires substantial amount of energy and special conditions such as high pressure and temperature [2,3]. It is possible to increase efficiency of the process using catalytic reformation under lower temperatures and increase production yields. Materials participating in the reaction must possess adequate CO₂ adsorption properties, provide with charge carriers with proper reduction and oxidation potentials for successful reformation of CO₂.

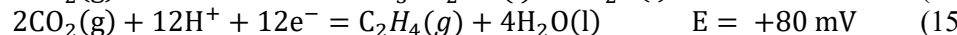
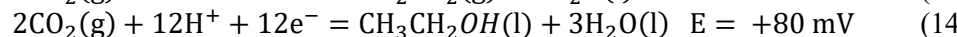
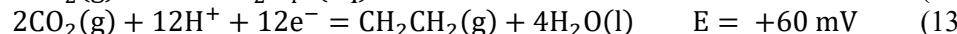
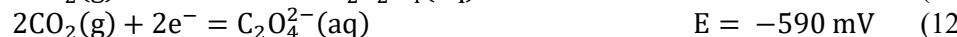
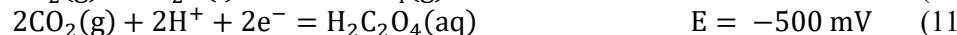
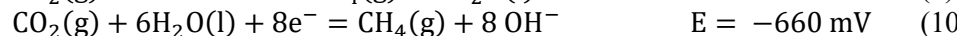
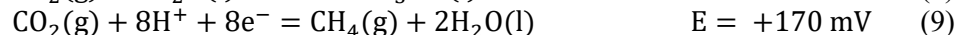
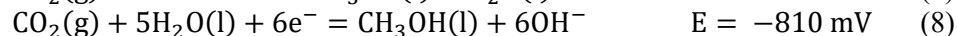
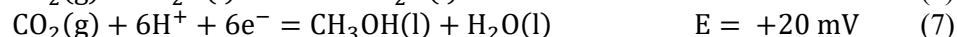
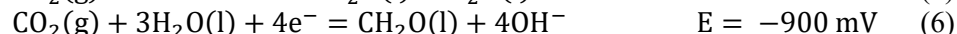
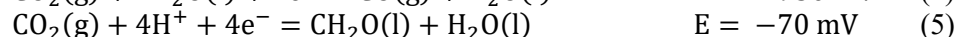
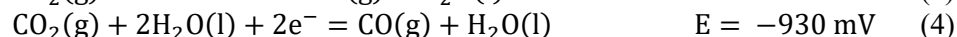
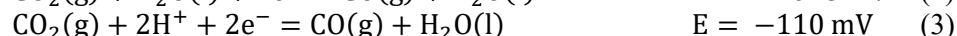
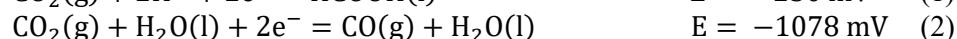
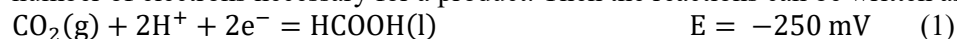


Various technologies and catalysts in different technology readiness levels are available or are under development, such as CuO loaded TiO₂ nanotubes for photocatalytic reformation [4] or electrocatalytic reduction on various forms of copper [5,6]. Estimation and more importantly determination of the efficiency of both electrocatalytic and photocatalytic reformation of CO₂ is necessary.

In this work review of reactions and efficiency of both processes based on existing technological methods was done.

2. Electrocatalytic process

CO₂ electrocatalytic reduction has been under investigation for decades, but many uncertainties still remain, such as the reformation pathway from CO₂ to higher hydrocarbons, electrolyte influence, etc. The question has been tackled by deWulf and Bard looking into copper electrode using electrochemical methods [7], Furet et al. investigation of silver thin films through spectroscopic methods [8], Shen et al. investigating cobalt protoporphyrin immobilized on a pyrolytic graphite [9] or Kuhl et al. investigating various metal surfaces [10]. It has come to classifications of CO₂ reduction products into two categories: 1) gaseous; 2) liquid products, requiring different physical separation and characterization/identification methodologies. On the other hand, the reformation reactions also can be classified by the required number of electrons necessary for a product. Then the reactions can be written as



here electrode potential E vs standard hydrogen electrode (SHE) in normal conditions [11–14].

We clearly see that hydrocarbons such as ethanol and ethylene reactions require multi-electron transfer. In addition, overpotential plays an important role in the propagation of a reaction, especially involving higher number of electrons. Other parameters, such as electrolyte composition and concentration, pH, temperature, catalyst crystalline facets, dopants, must be considered. For example, majority products on Ag is CO, Cd produces HCOO⁻, on the other hand, various forms of Cu can produce wide variety of products [11,12,15–17]. Let's assume interest in hydrocarbons, such as C₂H₄, then appropriate catalyst will be selected by majority product, faradaic efficiency (FE), overpotential and catalyst synthesis process.

In early work of Hori et al [18] the reformation of CO to CH₂ and C₂H₄ was discussed. Process was carried out at copper electrode in aqueous electrolyte. It was reported that CO electrocatalytic reduction didn't proceed as the cathodic currents were on scale of 10⁻⁵ Acm⁻² [18]. Nowadays the current densities reported are with magnitude of 10⁻² [19] and up to 10¹ [13].

In later work of Hori et al. it was pointed out that CO₂ must initially be reduced to CO, which is adsorbed on the catalyst. Only then further reformation to C₂ and C₃ products are possible. Investigation of pH showed that CH₄ production is promoted at low pH and C₂H₄ at high pH, due to increase in electrolyte concentration of KHCO₃. Dependency was explained as ⁻OH neutralization by nearby HCO₃⁻

. It is noteworthy that current densities for C_2H_4 and C_2H_5OH were reported independent of pH level [20].

Electrolyte concentration influence on FE and production of hydrocarbons was investigated by Zhong et al. where they suggested that higher electrolyte concentrations provide with lower overpotentials at the same time increasing H_2 production FE [21]. At the same time it was reported that C_2H_4 production is more favourable under low overpotentials [5]. Thus, indicating that if we are interested in C_2H_4 production, a catalyst with low overpotential must be chosen and an electrolyte with high pH level can be used, due to reported current density independence of pH. But high concentration and pH promotes H_2 production, that sometimes is considered the rate determining step.

It was proposed as H_2^+ (ads) or $H_{ads} + H^+$ in comparison with previously assumed $H_2^+(ads) + e^- \rightarrow H_2$, where H_2^+ (ads) is transition state. If carbon adsorption on electrode followed by OH electronation and not H_2^+ (ads) or $H_{ads} + H^+$ is the rate determining step for ethylene, a formation diagram was proposed (See Figure 1) [20].

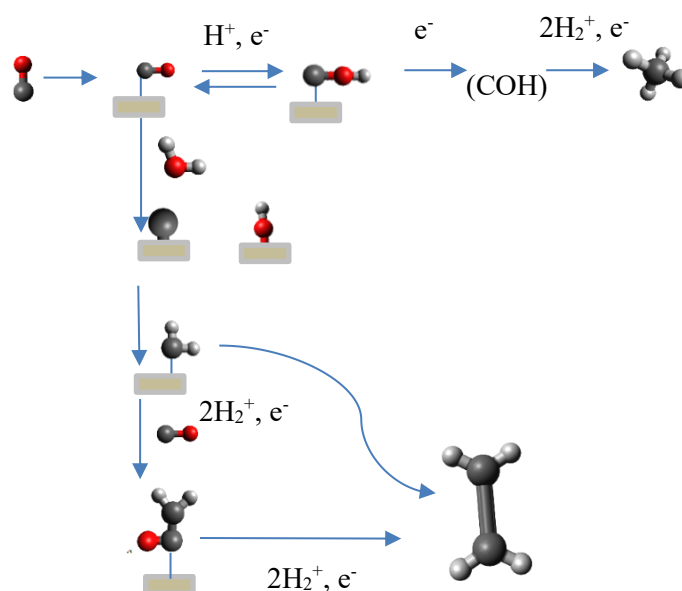


Figure 1. Reaction pathway of CO_2 reduction with intermediate adsorbed CO, COH, C and OH. Adopted from [20], molecules were drawn by using [24].

In case of pathway depicted in Figure 1, the rate determining step can be CO adsorption and following reformation into CH_4 in addition to various intermediates. It is noteworthy that other authors also came to similar conclusions and results for Cu nanoparticles [22,23].

Kortlever et al. suggested that CO_2 reduction can be viewed as multiple proton-electron reactions with products C1, C2+ and water, summarizing all probable product equations as equation (16) $kCO_2 + n(H^+ + e^-) \rightleftharpoons P + mH_2O$ (16) where P is the C1 and C2+ products [12].

Reaction involving more than 2 electrons (and protons) will involve intermediate steps, thus it will cause catalytic irreversibility. The role of intermediates in the CO_2 reduction was discussed. For example, ethylene formation starts with $*CO$ and $*CH_2$ intermediates, which follows abovementioned pathway [12]. But during investigation three unexplained observations were made. First, formation of methane from CO shows different pH dependency compared to ethylene. Second, often ethylene formation happened at more positive (less negative) potential without methane formation. Third, there is a structure sensitive and pH dependent pathways on Cu. Cu(111) reduction of CO to methane and ethylene is observed simultaneously, but on Cu(100) different pathway is observed, where only ethylene is formed, especially at high pH values [12]. On the electrode surface due to CO_2 reduction there is a

pH gradient that influences product selectivity. The pH value and ion presence can stabilize reaction intermediates, thus promoting formation of one or the other product [25]. Due to proton consumption during the reduction process and hydrogen evolution reaction (HER) the local pH at the electrode deviates from bulk, thus CO₂ can react with OH⁻ and form bicarbonate or carbonate [12]. On the other hand, Resasco et al. did an extensive investigation on production of CO, HCOO⁻, C₂H₄ and CH₃CH₂OH on Cu electrode, and concluded that the concentration of electrolyte anions has very little influence on production. Attributing it to lack of involvement of hydrogen atoms. At the same time providing with evidence for hydrogen and CH₄ production high sensitivity to anion concentration [26].

Malik et al [27] described electrochemical reduction of CO₂ process on various Cu morphologies, with FE of 26% at -2.75V. It was reported that grown dendrites on the surface capture some of gaseous products lowering overall efficiency. In addition, the use of Cu nanoparticles increased CO production, with selectivity dependence on size [27,28] attributing it to low-coordination site activity. Similar results concerning increase in CO production was found by Reske et al. decrease in particle size promotes H₂ and CO production, at the same time providing with higher current density in comparison with bulk Cu [28].

Authors investigation CO₂ reformation on metals as Fe, Au, Zn, Ni, Pt and Ag propose similar reformation pathway [29,30] as seen in Figure 1. Leading to conclusion that first step in CO₂ reformation is adsorption of CO₂, then CO is formed and desorbed or transformed into *CHO or *CHO species, that later forms into hydrocarbons as methane and methanol. It is noteworthy that metals as Pt, Pd, and Ni were reported to bind CO too strongly, which leads to electrode poisoning by *CO [25,31]. As previously mentioned crystallographic facets show selectivity for production: Cu (111) for CH₄ and Cu (100) for C₂H₄, suggesting that CO adsorption and lower surface energy is the reason of selectivity [27,32,33]. An overview of FE of different materials in various formations is presented in Table 1.

Table 1. FE and major product summary NP – nanoparticle, NW – nanowire, D – dendrite, NR – nanorods, NC – nanocubes, NF – nanoflowers,

Ref	Catalyst	electrolyte	pH	U, V vs RHE	FE	Product	Ref nr
Chen et al	Cu ₀ - Cu ₂ O	0.1M KHCO ₃	6.8	-1	32.1	C ₂ H ₄	[34]
Chen et al	Cu ₀ - Cu ₂ O	0.1M KHCO ₃	6.8	-1	16.4	C ₂ H ₅ OH	[34]
Chen et al	Cu ₂ O-PdClx	0.1M KHCO ₃	6.8	-1	30.1	C ₂ H ₆	[34]
Chen et al	Graphite-PdCl ₂	0.1M KHCO ₃	6.8	-1	4.7	HCOO ⁻	[34]
Chen et al	Graphite-PdCl ₂	0.1M KHCO ₃	6.8	-1	8.1	CO	[34]
Chen et al	Graphite-PdCl ₂	0.1M KHCO ₃	6.8	-1	0.2	CH ₄	[34]
Hori et al	Cu	KCl	5.9	-1.44	47.8	C ₂ H ₄	[5]
Hori et al	Cu	KHCO ₃	6.8	-1.41	30.1	C ₂ H ₄	[5]
Tang et al	Cu NP				30	CO	[35]
Tang et al	Cu NP				35	C ₂ H ₄	[35]
Reske et al	Cu NP	0.1 M KHCO ₃	6.8	-1.1 V	20/70	CO/H ₂	[28]
Raciti et al	Cu NW			-0.6 V	30.7	HCOOH	[36]
Raciti et al	Cu NW	0.1M KHCO ₃		-0.4 V	60	CO	[36]
Chen et al	Cu mesocrystal	0.1M KHCO ₃		-0.99 V	81	C ₂ H ₄	[37]
Roberts et al	Cu NC	0.1M KHCO ₃		-0.6 V		C ₂ H ₆	[38]
Sen et al	Cu foam	0.5M KHCO ₃		-0.5 V	26	HCOOH	[39]
Sen et al	Cu smooth	0.5M KHCO ₃		-0.5 V	3	HCOOH	[39]
Sen et al	Cu foam	0.5M KHCO ₃		-0.9 V	37	HCOOH	[39]
Kas et al		0.1 M KHCO ₃	6.8	-1.1 V	40	C ₂ H ₆	[40]
Malik et al	Cu NR	0.5 M KHCO ₃		-2.75 V	24.5	CO	[27]

Malik et al	Cu D	0.5 M KHCO ₃		-3 V	7	C ₂ H ₆	[27]
Malik et al	Cu D	0.5 M KHCO ₃		-2.75 V	7	C ₂ H ₄	[27]
Malik et al	Cu octahedral	0.5 M KHCO ₃		-3,0 V	5	CO	[27]
Malik et al	Cu D	0.5 M KHCO ₃		-2,5 V	2,8	CH ₄	[27]
Lui et al	Sn/SnO ₂	0.5 M KHCO ₃	7.2	-1.4 V	70	HCOO ⁻	[41]
Mistry et al	Au/Cu NP	0.1 M KHCO ₃	6.8	-1.2 V	20	CO/CH ₄	[42]
Wang et al	Cu ₂ Cd/Cd/Cu	0.1 M KHCO ₃		-1.0 V	84	CO	[43]
Bernal et al	CuCo NP	0.1 M KHCO ₃		-1.1 V	11	HCOOH	[44]
Bernal et al	CuCo NP	0.1 M KHCO ₃		-1.1 V	7.5	CO	[44]
Yang et al	Co NF	0.1 M KHCO ₃		-0.456 V	63.4	Formate	[45]
Ge et al	SnO ₂			-0.8 V	80	CO/Formate	[46]
Kaneco et al	Cu NP with Pb	NaOH in CH ₃ OH	14	-2.3 V	80	HCOOH	[47]
Kaneco et al	Cu NP with Zn	NaOH in CH ₃ OH	14	-2.1 V	12	CH ₄	[47]
Cook et al	Cu on GDE	1 M KOH	14	-2.8 V	69	C ₂ H ₄	[48]

Particle size also influence not only selectivity but also FE. CuCo NP showed decrease in HER, with increase of Cu content NP. On the other hand increased Cu content lead to increase in production of CO and HCOOH [44]. Flower like structures were proven to improve production of formate up to 63% FE. From Table 1 we can see that Cu is promising material for CO₂ reformation. Similar results were presented by Zhang et al. not only for Cu, but also for Zn and Sn based catalysts [49].

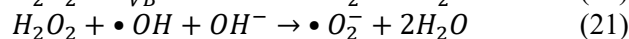
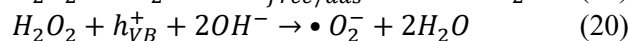
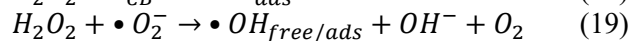
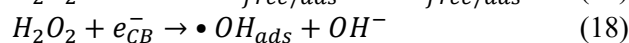
3. Photocatalytic CO₂ reduction

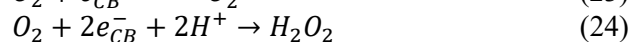
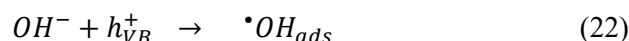
One of the problems in photocatalytic CO₂ reduction is that hydrogen donors, such as H₂O, CH₄, and alcohols, act as hole scavengers, thus it is necessary to separate reduction products from bulk electrolyte. This correlates with hydrogen production problems. Assuming that the CO₂ reduction reaction can proceed without limits set by charge carrier potentials (valence band (VB) and conduction band (CB) band position) [50].

Electrons are excited into the CB, with that, a hole is created in VB, where these charge carriers could be trapped in shallow or deep sites. In TiO₂ it could be Ti^{III}OH and Ti^{IV}OH^{*} shallow sites. Ti^{III} also could trap electrons in bulk material. If no site is found, charge carriers recombine and create excess heat on the material surface. Hydrocarbons can be produced only if hydride reductants are oxidized simultaneously. Thus, there is a need of oxidizing agents and oxidizing mechanism [50,51].

Direct oxidizing species are holes, but there are additional molecules with similar oxidizing properties: hydroxyl radicals (^{*}OH_{free} and ^{*}OH_{ads} [52]), superoxide (^{*}O₂⁻ [53]), singlet oxygen (^{*}O₂ [54]), also some authors report hydrogen peroxide and oxygen [55]. Karamian et al summarizes that ^{*}OH radicals are mostly product of surface hydroxyl and adsorbed water oxidation process. In this process peroxide can be produced and oxidized as described by equations (17) to (21).

Superoxides are supposed to be a weak oxidizing species as a product of one CB electron reduction of molecular oxygen or oxidizing hydrogen peroxide by VB hole (equation 22 to 24), whereas single oxygen is a strong oxidant and can be a product of ^{*}O₂⁻ and a trapped hole, though it has a short lifetime 2 μs on the surface, especially compared with hydroxyl radical with lifetime 5 times longer [50,54,55].





It must be remembered that CO₂ is very stable molecule, difference between lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital states is 13.7 eV. Adsorption of CO₂ onto catalyst is the best way to lower its energy due to the bend in LUMO level. One electron transfer initiates the adsorption and following chemical reactions. Electron or proton transfer provides with C-O bond breaking and C-H bond creation. It is believed that capturing electron from CB of photocatalyst is the first step in $\cdot CO_2^-$ anion radical as described in the following equation (25). Additional reductant is necessary, it is supposed that carbon-free reductants such as H₂ or water allow C1 products and carbon containing reductants such as CH₄ can promote C2, C3 products [50].



P-type photocathodes and earth-abundant n-type anodes such as WO₃, Fe₂O₃, TiO₂ can be used for photocatalytic CO₂ reduction. By utilizing metallic and composite catalysts as cathodes one can gain high FE and products as CH₄ and C₂H₄. In a photocatalytic cell using WO₃ and Cu or Sn/SnO_x electrodes CO₂ reduction potential of -3.0 V and +0.2V vs Reversible hydrogen electrode (RHE) has been reported. Thus the photocatalytic CO₂ reduction is described by equations (1)-(15) with lower bias potential due to photocatalytic charge carrier generation [56]. FE and necessary bias potentials for photocatalytic CO₂ reduction are provided in Table 2.

Table 2 Summary of FE and bias potentials in photocatalytic CO₂ reduction.

Ref	Catalyst	electrolyte	pH	Potential V vs RHE	FE	Product	Ref nr	λ , nm
Magesh et al	WO ₃ -Cu	KHCO ₃	7.5	+0.87	42.3	CH ₄	[57]	>420
"_"	WO ₃ -Cu	KHCO ₃	7.5	+0.65	64.6	CH ₄	[57]	>420
"_"	WO ₃ -Cu	KHCO ₃	7.5	+0.75	67	CH ₄	[57]	>420
"_"	WO ₃ -Cu	KHCO ₃	7.5	+0.87	4	C ₂ H ₄	[57]	>420
"_"	WO ₃ -Cu	KHCO ₃	7.5	+0.65	4.5	C ₂ H ₄	[57]	>420
"_"	WO ₃ -Cu	KHCO ₃	7.5	+0.75	2.7	C ₂ H ₄	[57]	>420
"_"	WO ₃ -Sn/SnO _x	KCl	7.5	+0.6	27.5	HCOOH	[57]	>420
"_"	WO ₃ -Sn/SnO _x	KCl	7.5	+0.7	27.5	HCOOH	[57]	>420
"_"	WO ₃ -Sn/SnO _x	KCl	7.5	+0.8	26.8	HCOOH	[57]	>420
Hinogami et al	p-Si	0.1 M KHCO ₃	6.8	-0.62	12	CO	[58]	>420
"_"	Cu/p-Si	0.1 M KHCO ₃	6.8	-0.52	25	CH ₄	[58]	>420
"_"	p-Si	0.1 M KHCO ₃	6.8	-1.026	73.5	H ₂	[58]	>420
"_"	Ag	0.1 M KHCO ₃	6.8	-1.49	75.9	CO	[58]	>420
"_"	part-Ag/p-Si	0.1 M KHCO ₃	6.8	-0.806	50.9	CO	[58]	>420
"_"	Au	0.1 M KHCO ₃	6.8	-0.966	82.2	CO	[58]	>420
"_"	part Au/p-Si	0.1 M KHCO ₃	6.8	-0.496	62.2	CO	[58]	>420
Yoneyama et al	p-CdTe	0.1 M Na ₂ CO ₃	n.a.	-0.55	48.4	HCOOH	[59]	>450
"_"	p-CdTe	0.1 M TEAP	n.a.	-0.55	65.6	CO	[59]	>450
"_"	p-InP	0.1 M TEAP	n.a.	-0.55	17.5	HCOOH	[59]	>450
"_"	p-InP	0.1 M Na ₂ CO ₃	n.a.	-0.55	36.2	HCOOH	[59]	>450
Tan et al	5GO-OTiO ₂	Gaseous CO ₂ with H ₂ O	n.a.	0	3.45	CH ₄	[60]	>400

“-“	5GO-OTiO ₂	Gaseous CO ₂ with H ₂ O	n.a.	0	9.07	CO	[60]	>400
“-“	5GO-OTiO ₂	Gaseous CO ₂ with H ₂ O	n.a.	0	1.75	C ₂ H ₄	[60]	>400

4. Conclusions

Catalytic CO₂ reformation is yet to be fully understood. The pathways of electrocatalytic and photocatalytic reduction are similar but requires different parameter control and thus have different production efficiency.

In electrocatalytic reduction higher hydrocarbons are produced under more negative overpotentials than -1.3 V vs NHE. Low carbonate and KCl concentrations provide higher FE for C₂H₄ formation. pH influence is not determined but results suggest that flow of electrolyte should be applied for higher FE.

Electrocatalytic CO₂ reduction in liquid electrolytes is characterized by higher production rates and photocatalytic reduction production volumes are substantially lower. Production of higher hydrocarbons is challenging in photocatalytic reduction, as the majority of products are C1 and C2. In addition, in many cases photocatalytic CO₂ reduction requires bias potential, which increases overall energy consumption. It is necessary to investigate materials that would allow CO₂ reduction without bias potential. Photocatalytic processes are not able to deliver high enough current densities for high volume production.

If the goal is C₂H₄ then nanostructured Cu should be chosen as catalyst material, higher concentration electrolyte should be used in electrocatalytic CO₂ reformation.

5. Acknowledgement

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