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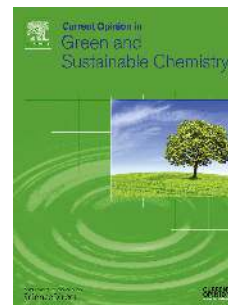
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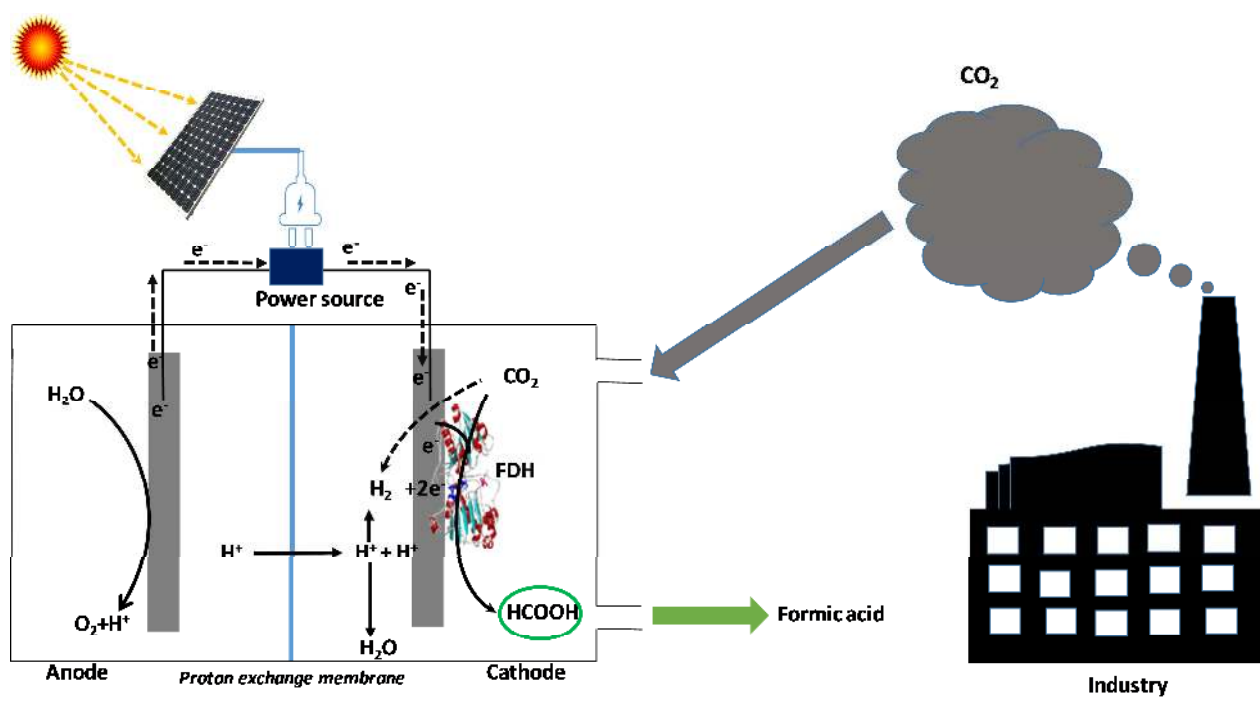
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Graphical Abstract



Current Trends in Enzymatic Electrosynthesis for CO₂ Reduction

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Abstract

Enzymatic electrosynthesis offers a novel approach to the production of chemicals through CO₂ sequestration. In this mini-review, we present the most recent state-of-the-art information on enzymatic CO₂ reduction for the production of chemicals such as formic acid using oxidoreductase (single or multiple) enzymes as electrocatalysts in enzymatic electrosynthesis cell (EEC). Key challenges towards upscaling of this CO₂ utilization approach are identified and future research directions are discussed briefly.

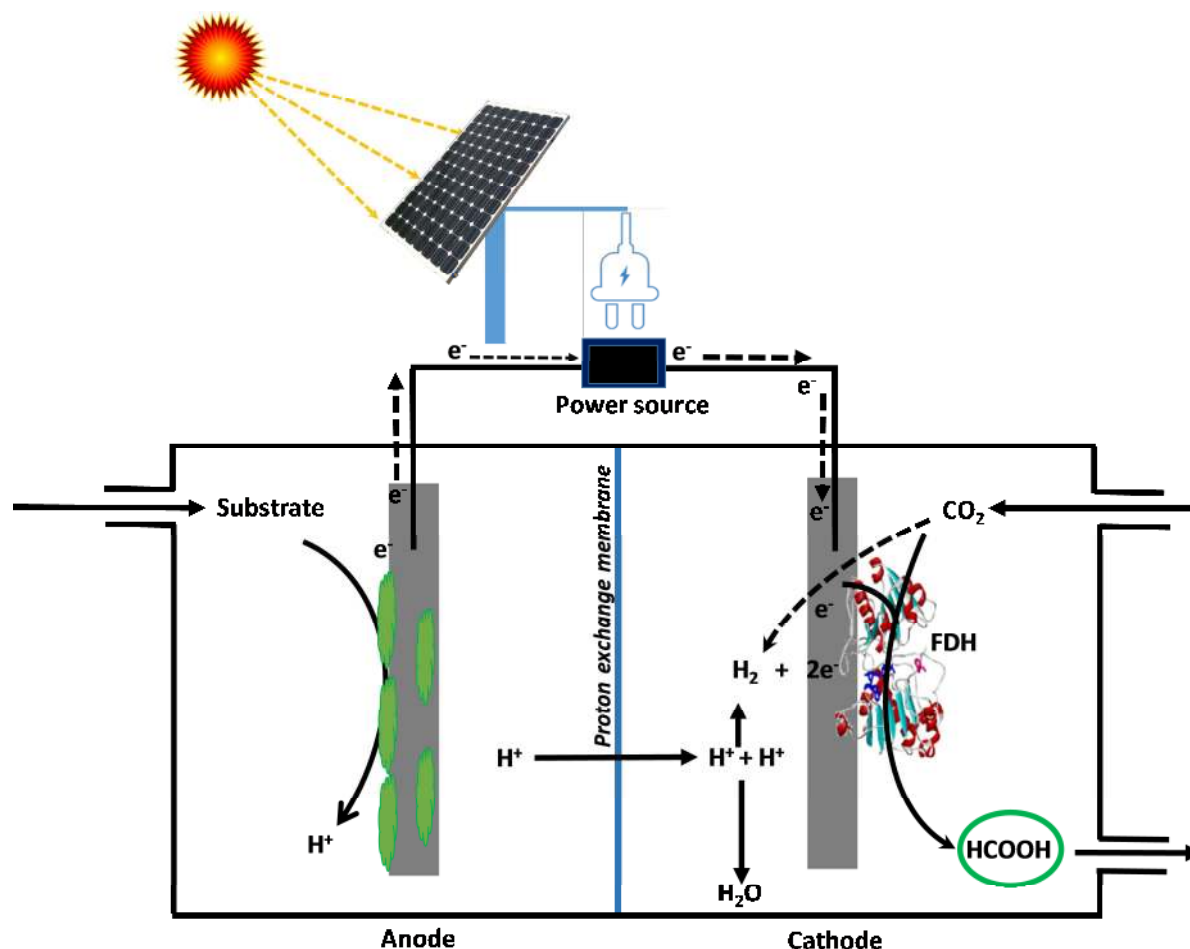
Key words: Enzymatic electrosynthesis, formic acid, oxidoreductase, CO₂ reduction

1. Introduction

Climate change due to the precipitous increase in greenhouse gas emissions particularly CO₂ in the atmosphere is driving the interest in developing carbon capture and utilization (CCU) technologies. CO₂ is the major carbon source which can be transformed into useful chemicals and fuels using different CCU technologies. Biological conversion of CO₂ is considered as a viable and sustainable approach for transitioning the existing linear carbon economy into a circular one in a highly desired biorefinery framework. The major biological CO₂ conversion approaches include microalgae cultivation, gas fermentation and microbial electrosynthesis [1-5]. The former is based on the use of algae and photosynthetic bacteria, whereas the latter two use chemolithoautotrophic microbial catalysts. Microbial electrosynthesis is an electricity-driven CO₂ reduction process catalyzed by microorganisms at the cathode of the bioelectrochemical systems [6]. Although the use of the whole cell microbial catalysts offers some important advantages, it also brings along several metabolism and process-related challenges. For instance, it results in less productivity due to the mass transport losses during the translocation of redox mediators across the cellular membrane and activation losses during the long electron transfer pathways [7].

Enzymatic electrosynthesis is another bioelectrochemical CO₂ reduction approach which is based on the use of specific enzyme catalysts instead of whole cell biocatalysts (Fig. 1).

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Figure 1: Schematic representation of a typical enzymatic electrosynthesis cell.

5 The renewable energy systems can supply the electrical energy needed to facilitate the
 6 reduction reactions at the cathodes. The use of specific enzymes to catalyze the cathodic CO₂
 7 reduction to produce specific products overcomes different losses. It is mainly due to the
 8 absence of interferences and intrinsic resistances along with the cost-effective downstream
 9 process [8-10]. Enzymatic electrosynthesis can thus be a remarkably energy efficient process.
 10 In this process, single or multiple enzyme (cascade-type) catalysts can be used depending
 11 upon the target product [11].

12 A major fraction of enzymes involved in CO₂ reduction discovered to date belongs to the
 13 oxidoreductase family and carbonic anhydrase (CA) [12,13]. These enzymes are vital for a
 14 vast choice of reactions in biological systems, primarily redox reactions. Usually, these
 15 enzymes exhibit a ping-pong mechanism where addition or loss of electrons and few atoms
 16 (involved in oxidation or reduction) are dispensing the unsteady enzyme form. Further, the
 17 enzyme gets to its unchanged form upon completing the reaction. This reaction is often
 18 accelerated by cofactors such as PQQ, FAD, heme and transition metals that bind firmly to
 19 the enzyme or a co-substrate such as NADP⁺, NAD⁺, and FMN that bind temporarily for
 20 short-duration to accomplish the reaction. These cofactors or chemical species loose or gain
 21 temporarily stored electrons to proceed with the redox reaction [14-16]. In recent times, the
 22 most studied single enzyme process has been the synthesis of formic acid from CO₂ reduction
 23 [10] using formate dehydrogenases (FDH) along with co-factor NADH [17, 18]. CA has been

1 used for less energy-intensive desorption of CO₂ scrubber for solvent recovery [19, 20]. The
 2 multi-enzyme approach is more advantageous over the single enzyme systems. It
 3 facilitates high CO₂ solubility (HCO³⁻) by CA in the aqueous phase. Later HCO³⁻ is converted
 4 to formic acid by FDH [21].

6 2. Recent advancements in Enzymatic electrosynthesis from CO₂

7 A classic enzymatic electrosynthesis cell (EEC) consists of enzymatic bioanode and
 8 biocathode (electrocatalysts) separated by electrolyte or gel or polymer and an external circuit
 9 with the load or power supply. Solid electrodes of different materials act as conductors and
 10 support the enzymes immobilization. The electrocatalysts used in EEC are oxidoreductase
 11 enzymes - a class of enzymes that catalyze redox reactions. Since these enzymes are selective
 12 electrocatalysts, careful selection of the specific enzyme is critical for the conversion of CO₂
 13 to chemicals. Formic acid production has been the main target process thus far due to its
 14 commercial importance [22]. Other target products include methane or methanol [23]. Very
 15 limited research work has been reported since the last two years on enzymatic
 16 electrosynthesis of formic acid from CO₂ reduction at cathode using FDH as a catalyst and
 17 NADH as an electron shuttle (Table 1).

18
 19 **Table 1. A consolidated table on the formic acid production in the enzymatic**
 20 **electrochemical cell through CO₂ reduction**

S. No	System	Enzyme	Enzyme Source	Cathodic reaction	Product	Maximum Concentration/ production rate	Ref.
1	EEC	FDH+CA	<i>Candida boidinii</i> (FDH)+ bovine erythrocytes (CA)	CA increases the solubility of CO ₂ + FDH reduces CO ₂ to formic acid with NADH e- shuttle	Formic acid	86.26 mg L ⁻¹ h ⁻¹	[10]
2	Hybrid MFC-EFC system	<i>Cb</i> - FDH	<i>Candida boidinii</i>	FDH reduces CO ₂ to formic acid with NADH e- shuttle	Formate	60 mg L ⁻¹ h ⁻¹	[24]
3	EEC	Hdr-SC	<i>Methanococcus maripaludis</i>	FDH reduces CO ₂ to formic acid with Hdr-SC e- shuttle	Formate	12 mg L ⁻¹ h ⁻¹	[25]
4	EEC	FDH	<i>Candida boidinii</i>	FDH reduces CO ₂ to formic acid with NADH e- shuttle	Formic acid	225.81 mg L ⁻¹ h ⁻¹	[26]
5	Electro-enzymatic system	RcFDH	<i>Rhodobacter capsulatus</i>	RcFDH reduces CO ₂ to formic acid with methyl viologen (MV) e- shuttle	Formate	276 mg L ⁻¹	[27]
6	Electro-enzymatic system	molybdenum-FDH (Mo-FDH)	<i>Escherichia coli</i>	Mo-FDH reduces CO ₂ to formate with Cobaltocene e ⁻ shuttle	Formate		[34]

7	Microbial electrosynthesis system (MES)	FDH	<i>Ralstonia eutropha</i>	neutral red (NR) and NADH	poly(3-hydroxybutyrate) (PHB)	485 ± 13 mg L ⁻¹	[38]
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2 A recent study by Zhang and coworkers investigated enzymatic electrosynthesis of formate
3 from the CO₂ reduction in a hybrid microbial fuel cell-enzymatic fuel cell (MFC-EFC)
4 system. Electrons were harnessed by the degradation of organic pollutants present in the
5 wastewater by anodic electrochemical active bacteria in MFC. In the same system,
6 immobilized cathode surface with FDH extracted from *Candida boidinii* was used along with
7 electro-polymerization and NADH to increase the electrochemical property. The production
8 of formate from NaHCO₃ as the CO₂ source was studied at lowered overpotentials as low as
9 0.1 V by connecting the MFC stack in different connection modes (i.e., series and parallel)
10 for external power supply. These authors achieved a maximum formate production rate of 60
11 mg L⁻¹ h⁻¹ with 70% Faradaic efficiency [24]. For the first time, Lienemann and colleagues
12 identified and studied the multi-enzyme heterodisulfide reductase supercomplex (Hdr-SC) in
13 *Methanococcus maripaludis* for rapid formate production. They reported that Hdr-SC
14 catalyze the methanogenesis via direct electron uptake with fast H₂ and formate production in
15 electrochemical reactors at -800 mV vs. Ag/AgCl applied potential. Formate production with
16 90% coulombic efficiency after five days was achieved [25].

17
18 A recent study by Srikanth et al. reported optimized potential (-0.8 V) for CO₂ reduction to
19 formic acid with 12.74% current efficiency at a production rate of 225.81 mg L⁻¹ h⁻¹. In this
20 study, an enzymatic electrosynthesis cell consisting of a H-type two-chambered reactor with
21 anode and cathode was used. The graphite-based cathode was immobilized with FDH as a
22 biocatalyst to convert CO₂ to formic acid. The major limitation of the study was denaturation
23 of the enzyme which limited the production time for 40 min due to non-recycling of the
24 proton donor NADH [26]. With this basic understanding, the same group continued testing
25 the formic acid production using FDH alone and in combination with CA in a dual
26 chambered enzymatic electrochemical cell. It consisted of CO₂ reducing cathode [cold rolled
27 graphite-polytetrafluoroethylene (PTFE) composite layer on a stainless-steel mesh, VITO[®]
28 CORE type electrode] and a platinum wire as the anode. CA was used to increase the
29 solubility of CO₂ and to enhance the formic acid production with both free and immobilized
30 forms (FDH, FDH+CA) on a cold rolled electrode based on graphite powder. Higher
31 production rate (43.13 mg L_{CO₂}⁻¹) and titer (647 mg L⁻¹) were obtained with FDH+CA free-
32 form than other variations studied. Authors identified large variation in the reduction current
33 operation with free form [(-6.2:3.9) Am⁻²], whereas the immobilized form showed less
34 variation [(-3.8:0.5) Am⁻²] due to increased enzyme stability. Moreover, the reproducibility of
35 the data reflected the longevity of the enzyme after immobilization. The addition of CA with
36 FDH increased the consumption of the current in both forms because it allowed rapid
37 dissolution of CO₂, which made it available for the catalytic reaction to increase formic acid
38 production [10]. Choi and co-workers selected O₂ stable FDH, isolated from *Rhodobacter*
39 *capsulatus* RcfDH) and studied with a different mediator (44 μMof alizarin red S (ARS),
40 anthraquinone-2-sulfonic acid (AQ2S), benzyl viologen (BV), and methyl viologen (MV))
41 for effective electron transfer to reduce CO₂. An electro-enzymatic system with RcfDH with
42 MV showed an effective CO₂ reduction of 6 mM of formate in 5 hours [27]. A novel CA
43 coated pectin membrane was developed, and its behavior studied for the first time by
44 Nemestóthy and colleagues in the field of membrane technology to separate CO₂/N₂. Authors

1 prepared a supported liquid membrane (SLM) and identified [Bmim] [NTf₂] ionic liquid (IL)
2 filled with cellulose acetate in the pores for solvent support during SLM fabrication on the
3 enzyme which in turn, caused a quick loss of initial biocatalyst activity. A 3-fold
4 enhancement in higher transmembrane pressures compared to control was observed after
5 improved resistance against high pressure of nearly 7.2 bar. Performance of the CA coated
6 pectin membranes tested with single and mixed gases of CO₂ and N₂ showed markedly
7 increased CO₂ permeability by 93 Barrer, whereas, N₂ remained unaffected [28]. Jin et al.
8 worked on metalorganic frameworks (MOFs) (ZIF-100 and CFA-1) mimicking CA (Zn as an
9 active center in metalloprotein) for effective CO₂ conversion. Authors revealed that MOFs
10 were more efficient for in situ CO₂ conversion than porous materials viz., MCM-41 and
11 activated carbon [29].

12 In addition to the above-mentioned enzymatic CO₂ conversion, Wang and co-researchers
13 have explored carbon monoxide dehydrogenase (CODH) for CO₂ conversion. In this study
14 researcher screened two different CODH using protein-film electrochemistry and evaluated
15 them in the presence of CO₂ [30]. Hansen et al. assessed the enzymatic electrochemical
16 approach based on the reduction of CO₂ to CO due to central metals in CODH [31]. Amao
17 and Shuto defined the electron shuttling with methyl viologen in enzymatic electrochemical
18 reactions and studied the artificial photosynthesis approach for CO₂ reduction. In this study
19 FDH was coupled to methyl viologen with a long alkyl chain, in turn allied to an indium tin
20 oxide (ITO) electrode. This approach for an artificial photosynthesis route, also includes
21 formate production from CO₂ [32]. Minteer and co-workers recently studied the multienzyme
22 approach to transfer electrons in a cascade way to generate biofuel. In this study, methanol
23 was produced by coupling ADH to NADH regeneration [33]. Bassegoda et al. worked on the
24 heterogeneous enzymatic electrochemical reduction of CO₂ to formate avoiding a co-factor.
25 In the same study, they also focused on active metal site of molybdenum-FDH and revealed
26 highly electrochemically active site than tungsten- FDH in the conversion of CO₂ to formate
27 [34]. Yuan et al. took the lead from previous understanding on active metal site of
28 molybdenum-FDH (Mo-FDH) and extended his work to using Mo-FDH from *Escherichia*
29 *coli* on the surface of a carbon electrode. In this case, cobaltocene (grafted to poly-
30 (allylamine), Cc-PAA), a low-potential redox polymer was used as an electron mediator for
31 efficient CO₂ reduction. During this study authors achieved 99.5% Faradaic efficiency at 0.66
32 V (vs. SHE) applied potential [35]. Understanding of heterogeneous enzymatic
33 electrochemical catalytic reduction of CO₂ led to another product formation other than
34 formate. Schlager and coworkers immobilized carbon felt electrode with all the three DH
35 encapsulated alginate matrix avoiding co-factors and studied the reduction of CO₂ to
36 methanol with 40% Faradaic yield [36, 37]. Chen and co-researchers also worked on poly(3-
37 hydroxybutyrate) (PHB) production with genetically engineered ribulose-1,5-bisphosphate
38 carboxylase/oxygenase (Rubisco) in *Ralstonia eutropha* to enhance CO₂ fixation. Reactor
39 systems were operated at a constant potential of -0.6 V vs. Ag/AgCl with FDH, neutral red
40 (NR) and NADH along with genetically modified *R. eutropha* at the cathode. This approach
41 showed high PHB production than control system (wild-type *R. eutropha* absence of FDH
42 and NR) [38].

43

44 3. Key challenges and future research directions

45 Despite the low yields, the most reported chemical compound in enzymatic electrosynthesis
46 cell is formic acid production by CO₂ reduction. Most importantly, the research work in this
47 area has been rather limited so far. Several challenges are foreseen towards practical

1 applicability of enzymatic electrosynthesis cell for formic acid production or other chemical
2 products such as CO, methane, and bicarbonate from CO₂ reduction. Identifying the suitable
3 and efficient microorganisms to produce enzymes and catalyze the reduction reactions
4 efficiently are the prime challenges that need to be addressed. Apart from that fundamental
5 challenges like high ohmic and activation losses, concentration over-potentials at the cathode
6 need to be reduced for efficient CO₂ conversion. Another important challenge in engineering
7 aspects is to design an economically viable enzymatic electrochemical system for
8 CO₂ conversion into liquid fuels and chemicals. Other challenges include cofactor enzyme
9 generation system and efficient hydration of CO₂ in water. The long-term stability of enzyme
10 catalysts also needs to be considered to make the system work for longer times. Towards the
11 enhancement of the catalytic reaction, efficient approach for the preparation of enzymes,
12 optimization of the reaction and stability mechanisms needs to be considered. The sensitivity
13 of the enzymes in harsh and high intense sunlight conditions, which decrease the enzymatic
14 activity is another area that needs research focus. The cost related aspects include protein
15 purification which hinders the large-scale application of such enzymatic systems also needs
16 to be addressed.

17

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Highlights

Enzymatic electrosynthesis is a sustainable route for the conversion of CO₂ to chemical and fuels.

Formate dehydrogenase (FDH) and carbonic anhydrase (CA) are most studied enzymes.

Multi-enzyme systems are more efficient with high Faradic efficiency for conversion of CO₂ to product.