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Current trends in enzymatic electrosynthesis for CO_2 reduction

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Enzymatic electrosynthesis offers a novel approach to the production of chemicals through CO_2 sequestration. In this minireview, we present the most recent state-of-the-art information on enzymatic CO_2 reduction for the production of chemicals such as formic acid using oxidoreductase (single or multiple) enzymes as electrocatalysts in the enzymatic electrosynthesis cell. Key challenges toward upscaling of this CO_2 utilization approach are identified, and future research directions are discussed briefly.

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Introduction

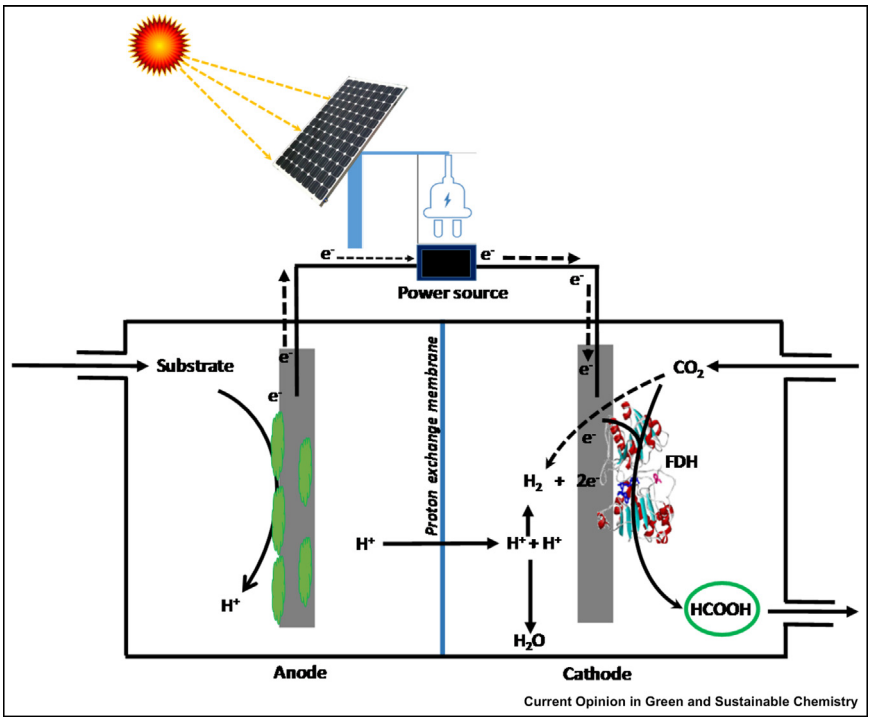
Climate change due to the precipitous increase in greenhouse gas emissions, particularly CO_2, in the atmosphere is driving the interest in developing carbon capture and utilization technologies. CO_2 is the major carbon source, which can be transformed into useful chemicals and fuels using different carbon capture and utilization technologies. Biological conversion of CO_2 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 CO_2 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 CO_2 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 CO_2 reduction approach, which is based on the use of specific enzyme catalysts instead of whole-cell biocatalysts (Figure 1).

The renewable energy systems can supply the electrical energy needed to facilitate the reduction reactions at the cathodes. The use of specific enzymes to catalyze the cathodic CO_2 reduction to produce specific products overcomes different losses. It is mainly due to the absence of interferences and intrinsic resistances along with the cost-effective downstream processes [8–10]. Enzymatic electrosynthesis can thus be a remarkably energy efficient process. In this process, single or multiple enzyme (cascade-type) catalysts can be used depending on the target product [11].

A major fraction of enzymes involved in CO_2 reduction discovered to date belongs to the oxidoreductase family and carbonic anhydrase (CA) [12,13]. These enzymes are vital for a vast choice of reactions in biological systems, primarily redox reactions. Usually, these enzymes exhibit a ping-pong mechanism where addition or loss of electrons and few atoms (involved in oxidation or reduction) are dispensing the unsteady enzyme form. Furthermore, the enzyme gets to its unchanged form on completing the reaction. This reaction is often accelerated by cofactors such as pyrroloquinoline quinone (PQQ), flavin adenine dinucleotide (FAD), heme, and transition metals that bind firmly to the enzyme or a cosubstrate such as nicotinamide adenine dinucleotide phosphate ($NADP^+$), nicotinamide adenine dinucleotide (NAD^+), and flavin mononucleotide (FMN) that bind temporarily for short duration to accomplish the reaction. These cofactors or chemical species lose or gain temporarily stored electrons to proceed with the redox reaction [14–16]. In recent times, the most studied single-enzyme process has been the synthesis of

Figure 1



Schematic representation of a typical enzymatic electrosynthesis cell. FDH, formate dehydrogenase

formic acid from CO_2 reduction [10] using formate dehydrogenases (FDHs) along with cofactor nicotinamide adenine dinucleotide-hydrogen (NADH) [17,18]. CA has been used for less energy-intensive desorption of CO_2 scrubber for solvent recovery [19,20]. The multienzyme approach is more advantageous over the single-enzyme systems. It facilitates high CO_2 solubility (HCO_3^-) by CA in the aqueous phase. Later, HCO_3^- is converted to formic acid by FDH [21].

Recent advancements in enzymatic electrosynthesis from CO_2

A classic enzymatic electrosynthesis cell consists of enzymatic bioanode and biocathode (electrocatalysts) separated by electrolyte or gel or polymer and an external circuit with the load or power supply. Solid electrodes of different materials act as conductors and support the enzyme immobilization. The electrocatalysts used in the enzymatic electrosynthesis cell are oxidoreductase enzymes—a class of enzymes that catalyze redox reactions. Because these enzymes are selective electrocatalysts, careful selection of the specific enzyme is critical for the conversion of CO_2 to chemicals. Formic acid production has been the main target process thus far owing to its commercial importance [22]. Other target products include methane or methanol [23]. Very limited research work has been reported since the last 2 years on enzymatic electrosynthesis of formic acid from CO_2 reduction at the cathode using FDH as a catalyst and NADH as an electron shuttle (Table 1).

A recent study by Zhang et al. investigated enzymatic electrosynthesis of formate from the CO_2 reduction in a hybrid microbial fuel cell (MFC)—enzymatic fuel cell system. Electrons were harnessed by the degradation of organic pollutants present in the wastewater by anodic electrochemically active bacteria in the MFC. In the same system, an immobilized cathode surface with FDH extracted from *Candida boidinii* was used along with electropolymerization and NADH to increase the electrochemical property. The production of formate from $NaHCO_3$ as the CO_2 source was studied at lowered overpotentials as low as 0.1 V by connecting the MFC stack in different connection modes (i.e. series and parallel) for external power supply. These authors achieved a maximum formate production rate of 60 mg L^{-1} h^{-1} with 70% Faradaic efficiency [24]. For the first time, Lienemann et al. identified and studied the multienzyme heterodisulfide reductase supercomplex in *Methanococcus maripaludis* for rapid formate production. They reported that the heterodisulfide reductase supercomplex catalyze the methanogenesis via direct electron uptake with fast H_2 and formate production in electrochemical reactors at −0.8 V (vs. Ag/AgCl) applied potential. Formate production with 90% coulombic efficiency after 5 days was achieved [25].

Table 1

A consolidated table on the formic acid production in the enzymatic electrochemical cell through CO_2 reduction.

S. No	System	Enzyme	Enzyme source	Cathodic reaction	Product	Maximum concentration/ production rate	Ref.
1	EEC	FDH+CA	*Candida boidinii* (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	*Cb*-FDH	*C. boidinii*	FDH reduces CO_2 to formic acid with NADH e^- shuttle	Formate	60 mg L^{-1} h^{-1}	[24]
3	EEC	Hdr-SC	*Methanococcus maripaludis*	FDH reduces CO_2 to formic acid with Hdr-SC e^- shuttle	Formate	12 mg L^{-1} h^{-1}	[25]
4	EEC	FDH	*C. boidinii*	FDH reduces CO_2 to formic acid with NADH e^- shuttle	Formic acid	225.81 mg L^{-1} h^{-1}	[26]
5	Electroenzymatic system	RcFDH	*Rhodobacter capsulatus*	RcFDH reduces CO_2 to formic acid with methyl viologen e^- shuttle	Formate	276 mg L^{-1}	[27]
6	Electroenzymatic system	Molybdenum-FDH (Mo-FDH)	*Escherichia coli*	Mo-FDH reduces CO_2 to formate with cobaltocene e^- shuttle	Formate		[34]
7	Microbial electrosynthesis system	FDH	*Ralstonia eutropha*	FDH (along with neutral red and NADH) used for formate production from CO_2; formate served as electron carrier for subsequent microbial conversion	Poly(3-hydroxybutyrate)	485 ± 13 mg L^{-1}	[38]

EEC, enzymatic electrosynthesis cell; MFC, microbial fuel cell; EFC, enzymatic fuel cell; FDH, formate dehydrogenase; CA, carbonic anhydrase; Hdr-SC, heterodisulfide reductase supercomplex; RcFDH, *Rhodobacter capsulatus*-FDH; Cb-FDH, *Candida boidinii*-FDH.

A recent study by Srikanth et al. reported optimized potential (−0.8 V *vs.* Ag/AgCl) for CO_2 reduction to formic acid with 12.74% current efficiency at a production rate of 225.81 mg L^{-1} h^{-1}. In this study, an enzymatic electrosynthesis cell consisting of a H-type two-chambered reactor with anode and cathode was used. The graphite-based cathode was immobilized with FDH as a biocatalyst to convert CO_2 to formic acid. The major limitation of the study was denaturation of the enzyme, which limited the production time for 40 min due to nonrecycling of the proton donor NADH [26]. With this basic understanding, the same group continued testing the formic acid production using FDH alone and in combination with CA in a dual chambered enzymatic electrochemical cell. It consisted of CO_2-reducing cathode (a cold rolled graphite–polytetrafluoroethylene composite layer on a stainless steel mesh, VITO® CORE type electrode) and a platinum wire as the anode. CA was used to increase the solubility of CO_2 and to enhance the formic acid production with both free and immobilized forms (FDH, FDH+CA) on a cold rolled electrode on the basis of graphite powder. Higher production rate (43.13 mg L_{CO2}^{-1}) and titer (647 mg L^{-1}) were obtained with FDH+CA free form than other variations studied. The authors identified a large variation in the reduction current operation with free form ([-6.2:3.9] Am^{-2}), whereas the immobilized form showed less variation ([-3.8:0.5] Am^{-2}) due to increased enzyme stability. Moreover, the reproducibility of the data reflected the longevity of the enzyme after immobilization. The addition of CA with FDH increased the consumption of the current in both forms because it allowed rapid dissolution of CO_2, which made it available for the catalytic reaction to increase formic acid production [10]. Choi et al. selected O_2 stable FDH, isolated from *Rhodobacter capsulatus*, and studied with a different mediator (44 μMof alizarin red S, anthraquinone-2-sulfonic acid, benzyl viologen, and methyl viologen [MV]) for effective electron transfer to reduce CO_2. An electroenzymatic system with FDH isolated from *R. capsulatus* with MV showed an effective CO_2 reduction of 6 mM of formate in 5 h [27]. A novel CA-coated pectin membrane was developed, and its behavior was studied for the first time by Nemestóthy et al. in the field of membrane technology to separate CO_2/N_2. The authors prepared a supported liquid membrane and identified [Bmim] [NTf2] ionic liquid filled with

cellulose acetate in the pores for solvent support during supported liquid membrane fabrication on the enzyme, which, in turn, caused a quick loss of initial biocatalyst activity. A threefold enhancement in higher transmembrane pressures compared with control was observed after improved resistance against high pressure of nearly 7.2 bar. Performance of the CA-coated pectin membranes tested with single and mixed gases of CO_2 and N_2 showed markedly increased CO_2 permeability by 93 Barrer, whereas N_2 remained unaffected [28]. Jin et al. worked on metalorganic frameworks (ZIF-100 and CFA-1) mimicking CA (Zn as an active center in metalloprotein) for effective CO_2 conversion. The authors revealed that metalorganic frameworks were more efficient for *in situ* CO_2 conversion than porous materials, viz. MCM-41 and activated carbon [29].

In addition to the aforementioned enzymatic CO_2 conversion, Wang et al. have explored carbon monoxide dehydrogenase (CODH) for CO_2 conversion. In this study, the researcher screened two different CODHs using protein film electrochemistry and evaluated them in the presence of CO_2 [30]. Hansen et al. [31] assessed the enzymatic electrochemical approach on the basis of the reduction of CO_2 to CO due to central metals in CODH. Amao and Shuto defined the electron shuttling with MV in enzymatic electrochemical reactions and studied the artificial photosynthesis approach for CO_2 reduction. In this study, FDH was coupled to MV with a long alkyl chain, in turn allied to an indium tin oxide electrode. This approach for an artificial photosynthesis route also includes formate production from CO_2 [32]. Addo et al. [33] recently studied the multienzyme approach to transfer electrons in a cascade way to generate biofuel. In this study, methanol was produced by coupling alcohol dehydrogenase (ADH) to NADH regeneration. Bassegoda et al. worked on the heterogeneous enzymatic electrochemical reduction of CO_2 to formate avoiding a cofactor. In the same study, they also focused on the active metal site of molybdenum-FDH (Mo-FDH) and revealed highly electrochemically active site than tungsten-FDH in the conversion of CO_2 to formate [34]. Yuan et al. took the lead from previous understanding on active metal site of Mo-FDH and extended his work to using Mo-FDH from *Escherichia coli* on the surface of a carbon electrode. In this case, cobaltocene (grafted to poly-(allylamine), Cc-PAA), a low-potential redox polymer was used as an electron mediator for efficient CO_2 reduction. During this study, authors achieved 99.5% Faradaic efficiency at 0.66 V (vs. SHE) applied potential [35]. Understanding of heterogeneous enzymatic electrochemical catalytic reduction of CO_2 led to another product formation other than formate. Schlager et al. immobilized carbon felt electrode with all the three DH encapsulated alginate matrix avoiding cofactors and studied the reduction of CO_2 to methanol with 40% Faradaic yield [36,37]. Chen et al. also worked on poly(3-hydroxybutyrate) production with genetically engineered ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) in *Ralstonia eutropha* to enhance CO_2 fixation. Reactor systems were operated at a constant potential of −0.6 V vs. Ag/AgCl with FDH, neutral red, and NADH along with genetically modified *R. eutropha* at the cathode. This approach showed high poly(3-hydroxybutyrate) production than control system (wild-type *R. eutropha* absence of FDH and neutral red) [38].

Key challenges and future research directions

Despite the low yields, the most reported chemical compound in the enzymatic electrosynthesis cell is formic acid produced by CO_2 reduction. Most importantly, the research work in this area has been rather limited so far. Several challenges are foreseen toward practical applicability of enzymatic electrosynthesis cell for formic acid production or other chemical products such as CO, methane, and bicarbonate from CO_2 reduction. Identifying the suitable and efficient microorganisms to produce enzymes and catalyze the reduction reactions efficiently are the prime challenges that need to be addressed. Apart from that, fundamental challenges such as high ohmic and activation losses and concentration overpotentials at the cathode need to be reduced for efficient CO_2 conversion. Another important challenge in engineering aspects is to design an economically viable enzymatic electrochemical system for CO_2 conversion into liquid fuels and chemicals. Other challenges include cofactor enzyme generation system and efficient hydration of CO_2 in water. The long-term stability of enzyme catalysts also needs to be considered to make the system work for longer times. Toward the enhancement of the catalytic reaction, efficient approach for the preparation of enzymes, optimization of the reaction, and stability mechanisms needs to be considered. The sensitivity of the enzymes in harsh and high-intense sunlight conditions, which decrease the enzymatic activity, is another area that needs research focus. The cost-related aspects, including protein purification which hinders the large-scale application of such enzymatic systems, also need to be addressed.

Conflict of interest statement

Nothing declared.

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