



Specific and sustainable bioelectro-reduction of carbon dioxide to formate on a novel enzymatic cathode



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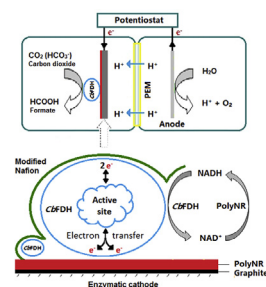
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HIGHLIGHTS

- Enzymatic functions of immobilized *Cb*FDH were secured by modified Nafion.
- Enzymatic electrosynthesis of formate was achieved at low overpotential.
- Two-electron transfer was confirmed in catalytic bicarbonate reduction to formate.
- Specific and sustainable formate production was obtained by a reusable biocathode.

GRAPHICAL ABSTRACT



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ABSTRACT

To specifically convert waste CO₂ into renewable chemicals, enzymatic electrosynthesis (EES) of formate from CO₂ reduction was investigated in a bioelectrochemical system (BES). A novel cathode with immobilized enzyme and electropolymerized mediator-regenerator was fabricated for such bioelectrocatalytic EES. Formate dehydrogenase from *Candida boidinii* (*Cb*FDH) was set as a new model enzyme in BES. Modified Nafion micelles with appropriate pore size were found to be suitable for immobilization of *Cb*FDH and protection of its enzymatic activity and lifetime at optimal pH of 6.0. The enzymatic electrosynthesis activity of immobilized *Cb*FDH was characterized systematically. Quite a small overpotential was required in the bioelectrochemical EES reaction. A two-electron transfer process was confirmed in the *Cb*FDH-catalyzed reduction of bicarbonate to formate. With electro-polymerized neutral red (PolyNR) as a NADH (mediator)-regenerator, efficient formate production could be achieved at a maximum rate of 159.89 mg L⁻¹ h⁻¹ under poised potential of -0.80 V (vs. SHE). The immobilized *Cb*FDH and electropolymerized PolyNR on an enzymatic cathode contributed greatly to sustainable EES, giving energy-rich formate as the only catalysis product.

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1. Introduction

Despite causing atmospheric pollution worldwide, the emitted

CO₂ can be utilized as an abundant carbon source for synthesis of hydrocarbon fuels. Conversion of CO₂ to formate (or formic acid), which is the first step in methanol or methane production route, is of particular interest in biofuel and practical bioenergy engineering. Various CO₂-reduction technologies have been well developed and investigated in depth till now (ElMekawy et al., 2016; Roy et al., 2016). Conversion of CO₂ by plants or algae can make use of

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energy-rich biomass to produce carbohydrates biofuels including formate. But this technology is impractical since it is at great energy expense. In physio-chemically catalytic reaction, CO₂ is inserted into a metal-and-hydrogen bond of organometallic complex to hydrogenate CO₂. This process, however, depends on the precious metals as catalysts under supercritical conditions (Hara et al., 1995; Hori, 2008). Comparatively, electrochemical reduction of CO₂ shows a great advantage in generating a variety of organic or inorganic compounds such as carbon monoxide, methane and lipids (Hu et al., 2015; Taher et al., 2015; Ganesh, 2016). Unfortunately, a major problem lies in current electrochemical approach due to the energy inefficiency at extreme electrode potentials and nonspecific conversion by giving a mixture of products.

To seek a more energy-efficient way of CO₂ conversion to formate, bioelectrochemical reduction has been proved to be applicable in aqueous solution under much less harsh conditions as compared with those required by chemical catalysts (Zhao et al., 2012; Li et al., 2013). The dissolved CO₂ species can be hydrogenated and thence reduced on a bioelectrode. Noticeable formate production can be detected at a lowered electrode potential in the presence of biocatalysts. Formate dehydrogenase (FDH), a class of purified enzymes, can prominently accelerate the electron transfer from formate to CO₂. The reverse reaction has long been expected to be catalyzed by some FDH. The active sites in FDH can promote oriented electron transfer, producing formate as the only reduction product. Nevertheless, limited types of FDH exclusively from anaerobic bacterium, e.g. only *S*FDH1 from *S. fumaroxidans* and *Ec*FDH-H from *E. coli*, have been reported to be capable of enzymatic electrosynthesis (EES) of formate from CO₂ till now (Reda et al., 2008; Choe et al., 2014). Formate production by FDH from *Candida boidinii* (*Cb*FDH), a commercially available enzyme, was rarely been investigated systematically in a bioelectrochemical system (BES) due to its low CO₂-reducing activity for EES.

One of the major challenges for *Cb*FDH-driven EES is the requirement for mediators and initiators to promote the reaction course. Nicotinamide adenine dinucleotide, an active coenzyme abbreviated as NAD⁺/NADH, can facilitate the electron transfer in metabolic processes of all living cells. It can also act as a mediator to accelerate the reversible CO₂-reduction reaction. Similar to the most common class of FDH, *Cb*FDH can catalyze the direct transfer of hydrogen from formate to NAD⁺, whereas the reversion is difficult. An external motivation, which was considerably lower than that required by widely used metal catalysts (Hori et al., 1994), can initiate the two-electron transfer to CO₂ species via the electrochemically active sites buried inside the *Cb*FDH framework. Therefore, it is crucial to construct a suitable system for enzymatic interactions with mediators and initiators.

Another challenge confronted with current EES is the limited lifetime of *Cb*FDH, which is crucial to be dealt with on an enzymatic electrode (Dominguez-Benetton et al., 2013). Recently, active lifetimes of fragile dehydrogenase enzymes have even been extended successfully through encapsulating them in micellar polymers (Moore et al., 2004). The polymeric micelles can physically confine the enzymes and protect them from denaturation by providing a biocompatible hydrophobic nest and buffered microenvironment. Nafion, a commercially perfluorinated sulfonate ionomer, contains hydrophobic regions that can be used to encapsulate enzymes (Addo et al., 2010). Nevertheless, neither the extremely tiny pore structure inside the micelles nor the acidic property of the sulfonic acid side chain makes it feasible for enzyme immobilization. Modified Nafion with quaternary ammonium salts, such as tetrabutylammonium bromide and triethylhexylammonium bromide with higher hydrophobicity, has been reported to depict enlarged pore size for better diffusion of protons, small cations or even some larger ions such as NAD⁺/NADH (Schrenk et al., 2002). In addition,

the neutralized Nafion created a membrane-like microenvironment to buffer pH changes within the pore structure for stabilizing enzyme, thus increased the enzymatic activity and effective lifetime (Karyakin et al., 2002). To the best of our knowledge, application of modified Nafion micelles in *Cb*FDH immobilization and protection has not been demonstrated yet.

To narrow the above-mentioned research gaps between laboratory experiments and practical engineering, we herein proposed the catalytic CO₂ reduction to formate by immobilized *Cb*FDH in EES. Nafion micelles were pretreated with proper quaternary ammonium salts to enlarge the pore size which were suitable for enzyme immobilization. Electro-polymerized neutral red, in a form of electrochemically active redox film on the surface of cathode, was employed to regenerate NADH for EES. A reusable composite enzymatic cathode, which was capable of continuous electrocatalytic reduction of CO₂ and/or electrosynthesis of formate, was then fabricated and investigated systematically.

2. Materials and methods

2.1. Bioelectrochemical system

EES was conducted in a bioelectrochemical system (BES) as shown in Fig. 1. The dual-chamber reactor consisted of a 20-mL cathode chamber and a 10-mL anode chamber. A rotating graphite disk (0.30 mm in diameter × 1.0 mm in thickness) was utilized as cathode/working electrode, while single platinum wire as anode/counter electrode and Ag/AgCl (in 3.5 M KCl, +0.197 V vs. SHE) as reference electrode. *Cb*FDH was immobilized onto the cathode by conductive polymer matrix (modified Nafion micelles). In the cathode chamber, reduction of CO₂ to formate took place by accepting the electrons and protons from anode in 100 mM phosphate buffered saline (PBS) containing (mg L⁻¹): Na₂HPO₄·2H₂O, 11,472 and NaH₂PO₄·H₂O, 4,904. In the anode chamber, protons and electrons were released from water splitting by using 100 mM

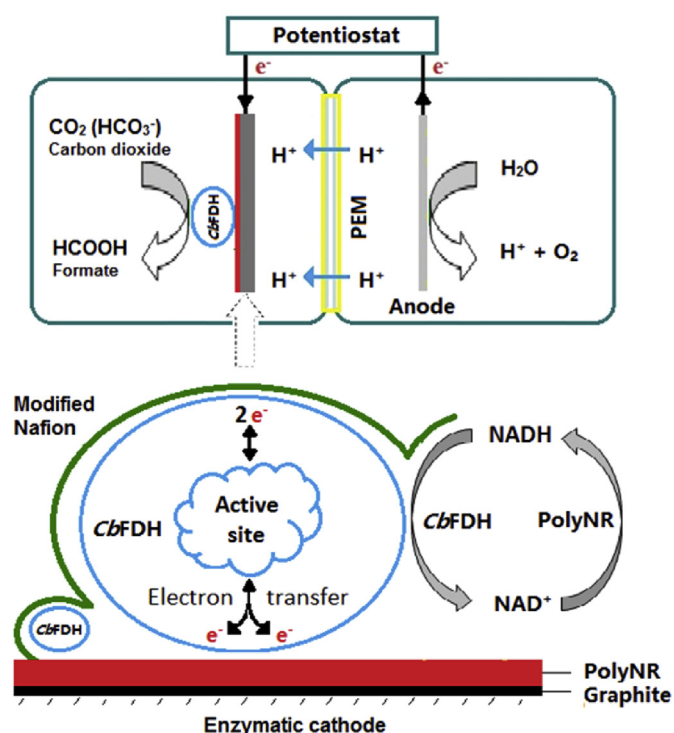


Fig. 1. Schematic diagram of a bioelectrochemical system with an enzymatic electrode.

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