

Opinion

Volume 3 Issue 5 – June 2017
DOI: 10.19080/AIBM.2017.03.555625

Adv Biotech & Micro

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Mechanisms of Charge Transfer during Bio-Cathodic Electro-Synthesis of CO₂-Neutral Methane



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Submission: May 15, 2017; Published: June 27, 2017

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Abstract

Exploiting fossil-fuels to meet the increasing per capita energy consumption is leading to generation of green house gasses. Massive CO₂ emission causes an alarming impact on global warming. Sustainable solutions are hence required to be explored to capture and re-utilize CO₂ to valuable products. Application of Bio-electrochemical systems (BES) is a novel approach based on electrochemical redox processes, capable of converting the chemical energy stored in biodegradable organic matter by catalytic activity of microorganisms to electrical energy or using electrical energy it can synthesis organic compounds from CO₂. This review briefly discusses the salient features of different electron transfer mechanisms and microbial pathways for cathodic generation of bio-methane in BES.

Keywords: Bio-electrochemical systems; Bio-methane; Extra-cellular electron transfer; Microbial electro-synthesis; Redox reactions

Introduction

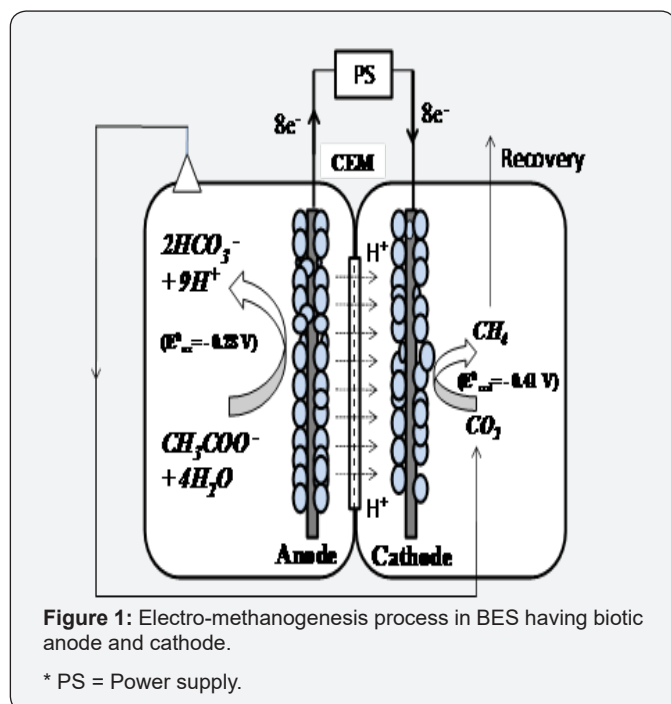


Figure 1: Electro-methanogenesis process in BES having biotic anode and cathode.

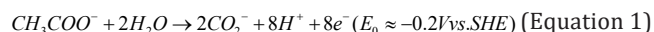
* PS = Power supply.

Bioelectrochemical approaches provide an attractive solution for microbial electro-synthesis of bio-methane, which is having a greater prospect to become an energy source and an energy

carrier as well [1]. Methane-producing bio-electrochemical system (BES) offers advantages of producing such CO₂-neutral methane (Figure 1), where the process is independent of biomass. Energy from the (excess) renewable electricity can be stored in the form of produced methane. One of the key principles of BES systems is the use of microorganisms as bio-catalyst, which helps in executing diversified bio-chemical reduction and oxidation reactions [2,3]. A more recent application of electron transfer from electrode to microorganisms, where current is getting consumed, enables the possibilities of biological reduction of oxidized pollutants in bioremediation systems [4-6], biological reduction of nitrate to nitrogen gas [7] and microbial electro-synthesis for production of a wide array of valuable fuels and reduced bio-chemical compounds [8,9].

Conversion of CO₂ to methane in bio-electrochemical system

Methane producing BES consists of both anodic and cathodic compartments, which were comprised of respective anodic and cathodic electrode and separated by proton exchange membrane. Oxidation of organic substrates takes place in the anodic chamber and the fate of oxidation reaction depends on the type of substrates used. For example, upon acetate oxidation, protons and electrons get liberated and the process generates two moles of carbon di-oxide (Equation 1).

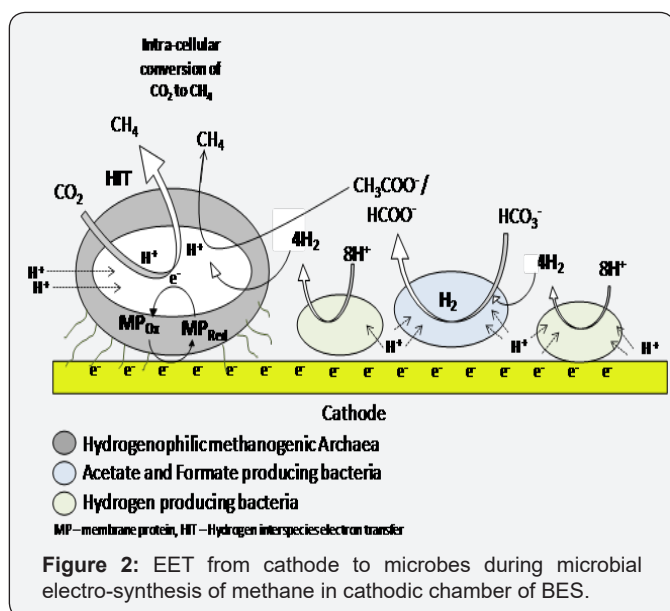
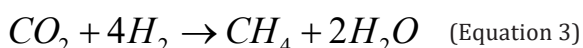
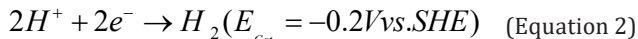


Electrons are transferred by redox active mediators or conductive bacterial pili to anode and flow through the external circuit to cathode; whereas, protons are transferred through membrane to maintain the electro-neutrality of the system. Application of bio-cathode in microbial electrolysis cells (MEC), a variant of BES, enables the growth of microorganisms, which catalyses the reduction of CO_2 generated in the anodic chamber, combined with electrons and protons, to generate methane. Methane generation by hydrogenotrophic methanogens takes place via two classical pathways of extracellular electron transfer (EET) [10].

Mechanisms of Extracellular Electron Transfer for Bio-Cathodic Methane Generation

Mediated electron transfer

In microbial electro-synthesis process, during mediated electron transfer, hydrogenotrophic methanogenesis is dependent on biotic/abiotic H_2 production (Figure 2). The intermediate H_2 production can be achieved electrochemically (Equation 2) or bio-electrochemically i.e., by the activity of hydrogenase enzyme present in electro-active H_2 producing microorganisms. The produced hydrogen then can be consumed by H_2 -utilizing methanogens in presence of excess CO_2 to produce methane under applied cathode potential of around -0.5 V vs. SHE (Equation 3) [3,11].



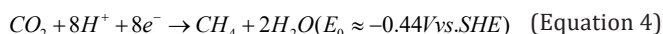
The major disadvantage of this process was found to be the use of expensive cathode catalyst for achieving enhanced electro-catalytic activity for H_2 evolution. Moreover, considering overpotential and internal resistance developed during electro-

hydrogenesis it requires 0.5-1V to carry out the process effectively. Bio-methane production can also be facilitated by acetate and formate producing bacteria (Figure 2), where the intermediate products are again re-utilized by methanogenic bacteria to produce methane as reaction end-product [12].

Microbial electrochemical synthesis

An investigation on direct metabolic pathways for EET driven methane production was first reported by Cheng et al. [13] where the ability of microorganisms to produce methane from CO_2 reduction by using an electrode as direct electron donor was depicted while using mixed methanogenic inoculum and referred to as electro-methanogenesis process (Figure 2). Reaction of electron transport is catalyzed by membrane-bound compounds, which can use the energy difference between donor and acceptor (depending on the difference in redox potentials, ΔE) and facilitate the establishment of ion-gradient across the membrane. Trans-membrane ion transport is assisted by membrane-localized protein complexes (such as cytochrome c and terminal oxidases/ reductases) or bacterial conductive pili (nano-wires), which can transport electrons to the final electron acceptors [14,15]. The standard potential for methane production via electro-methanogenesis ($E_{\text{cat}} = -0.24$ V vs. SHE at pH of 7) is lower than the H_2 production via indirect EET (electro-hydrogenesis, $E_{\text{cat}} = -0.41$ V vs. SHE), which makes the former reaction to be energetically more efficient to occur [10]. Hence, electro-methanogenesis can be carried out in a single-chamber anaerobic systems like UASB reactor to construct localized methane producing MECs, which can be regarded as a potentially applicable device to increase the overall methane yield [16].

The CO_2 and electrons generated in the anodic chamber during biological oxidation of organic matter can be reutilized during the cathodic generation of methane. The possible electrochemical reduction of CO_2 to CH_4 in the cathodic chamber happens according to the following equation (Equation 4):



Methane production at more negative potential within the range of -0.65 to -0.9 V vs. SHE, both via direct EET and abiotically produced H_2 gas via hydrogenotrophic methanogenesis, was compared and the relative contributions of these two mechanisms were reported to be highly dependent on the set cathodic potential [17]. It was also found that the biotic cathode with mixed enriched culture of biocatalyst enhanced current densities compared to the abiotic cathode and generated small amount of abiotic H_2 . However, the study could not reveal the inter-species H_2 transfer between electro-active H_2 producing microorganisms and H_2 utilizing methanogens.

Direct interspecies electron transfer

A more recent interest has been revealed on mechanisms by which exchange of electrons happens through electrically

conductive biological connections of filamentous appendages and conductive extra-cellular polymeric substances (EPS) present in the intercellular spaces of syntrophic microbial partners in the form of aggregates [8,18,19]. Such bacteria can therefore participate in direct interspecies electron transfer (DIET), which can be attributed by their ability to form extra-cellular electrical connections. The knowledge cultivation on DIET mechanism, which is yet to be explored completely, is important to understand the energy exchange and to expand the metabolic capabilities of anaerobic microbial community

The well-known mechanism of hydrogen interspecies electron transfer (HIT) depicts the ability of electron donating microbial species (hydrogen producing bacteria) to reduce protons to H₂, which is consumed by electron accepting partner species (methanogens) for reduction of any electron acceptor, such as CO₂ [20]. DIET has been documented among *Geobacter* sp. and between co-culture of *Geobacter* and methanogenic species [21,22].

Conclusion

Research on cathodic reaction in BESs exploiting bio-cathodic electro-synthesis of methane, as alternative fuel, has been intensified over the last few decades. However, detailed understanding on charge transfer mechanisms are immensely needed to bring an insight of bio-electrochemical approaches for methane generation and recovery. Moreover, many scientific and technical challenges are yet to be addressed to make this technology more eco-friendly, economical and feasible for commercial applications, which can be regarded as an important step to mitigate the future requirement of clean energy.

Acknowledgement

Authors sincerely acknowledge the Ministry of New and Renewable Energy, Government of India (Ministry sanction letter no. 10/14/2010-P&C, dated 26/03/2012) for providing fellowship to the first author.

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DOI: [10.19080/AIBM.2017.03.555625](https://doi.org/10.19080/AIBM.2017.03.555625)

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