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Research review paper

Bioelectrohydrogenesis and inhibition of methanogenic activity in microbial electrolysis cells - A review

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ABSTRACT

Microbial electrolysis cells (MECs) are a promising technology for biological hydrogen production. Compared to abiotic water electrolysis, a much lower electrical voltage (~0.2 V) is required for hydrogen production in MECs. It is also an attractive waste treatment technology as a variety of biodegradable substances can be used as the process feedstock. Underpinning this technology is a recently discovered bioelectrochemical pathway known as "bioelectrohydrogenesis". However, little is known about the mechanism of this pathway, and numerous hurdles are yet to be addressed to maximize hydrogen yield and purity. Here, we review various aspects including reactor configurations, microorganisms, substrates, electrode materials, and inhibitors of methanogenesis in order to improve hydrogen generation in MECs.

1. Introduction

Hydrogen is an important chemical feedstock for many industries, such as the fertilizer industry for ammonia synthesis, and the oil industry for the conversion of crude oils into transportation fuels. It is a valuable energy carrier widely used to power hydrogen fuel cells (Logan, 2004). However, most of the hydrogen is conventionally derived from fossil fuel-based resources, primarily natural gas, via chemical refinery processes (Milbrandt and Mann, 2009). Hence, its production is generally considered as environmentally unsustainable. Biological production of hydrogen (bio-hydrogen) is a potentially more sustainable alternative, especially when organic wastes are used as the process feedstock (Hallenbeck and Benemann, 2002).

One promising option for bio-hydrogen production is via "bioelectrohydrogenesis", which can be accomplished using an emerging technology platform known as bioelectrochemical systems (BESs) or microbial electrochemical technologies (METs) (Liu et al., 2005; Rozendal et al., 2006). BESs have been developed for a wide range of applications, including wastewater treatment, fuel gas production (H_2, CH_4), nutrient recovery, chemical synthesis, desalination and bioremediation (Sleutels et al., 2012). A key feature of this technology is that it employs microorganisms to catalyze redox reactions at conductive electrode surfaces. The most widely studied BESs are either microbial fuel cells (MFC), which aim to produce electricity; and microbial electrolysis cells (MECs), which aim to produce biogas or value added chemicals (Logan et al., 2008; Clauwaert and Verstraete, 2009; Chookaew et al., 2014). During the conversion of bio-waste into H_2, exoelectrogenic bacteria first oxidize (degrade) organic matter and transfer the electrons to a solid electrode (bioanode) (Fig. 2a). The electrons then travel through an external circuit and combine with protons at an anaerobic cathode resulting in the generation of hydrogen (Logan et al., 2008). Typically, the reducing power attainable with a bioanode is insufficient to drive the hydrogen evolution reaction (HER) at the cathode. However, by supplementing the process with a small voltage (normally ranging from 0.2 V to 1.0 V) the cathodic HER can be facilitated in a MEC (Reactions (1) & (2)). Since a much higher voltage (E^0 > 1.2 V) is required in conventional water electrolysis (Fig. 2b) processes (Reactions (3) & (4)), using MEC for bio-hydrogen production is considered as an energy-efficient option. Indeed, it has been reported that the energy requirement for MECs is only about 0.6 kWh m^{-3} (0.2 mol H_2 energy/mol-H_2 produced), whereas in water electrolysis 4.5–5 kWh m^{-3} is required (1.5–1.7 mol H_2 energy/mol-H_2 produced)

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(Logan et al., 2008; Cheng and Logan, 2007).

Microbial Electrolysis:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \; E_{anode} = -0.279\ V \quad (1)$$

$$2H^+ + 2e^- \rightarrow H_2 \; E_{cathode} = -0.414\ V \quad (2)$$

$$E^0 = E_{cathode} - E_{anode} = -0.135\ V$$

Water Electrolysis:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \; E_{anode} = 0.82\ V \quad (3)$$

$$2H^+ + 2e^- \rightarrow H_2 \; E_{cathode} = -0.414\ V \quad (4)$$

$$E^0 = E_{cathode} - E_{anode} = -1.22\ V$$

Further, waste materials other than fossil fuels are used as the feedstock to drive the HER, and the H_2 production rate can be $> 1\ m^3\ H_2\ m^{-3}\ d^{-1}$(11 mol H_2/mol glucose), which is three times higher than dark fermentation (Logan et al., 2008; Wang and Ren, 2013).

These features collectively make MECs a promising topic for research and development across the world, as reflected by the expanding volume of research outputs over the past decade (Fig. 1). Nonetheless, only a few review articles have discussed the use of MEC for hydrogen production and methanogenesis (Logan et al., 2008; Geelhoed et al., 2010; Kundu et al., 2013; Zhou et al., 2013; Zhang and Angelidaki, 2014; Kadier et al., 2014; Jafary et al., 2015; Escapa et al., 2016). A notable challenge to maximize hydrogen yields from MECs is the side production of methane via methanogenesis. Herein we discuss the currently available methods for the inhibition of methanogenesis in MECs, and highlight the use of chemical methanogenic inhibitors with the focus on their underpinning mechanisms at the enzymatic level. We suggest options of using these methanogenic inhibitors to improve the purity of the produced hydrogen from MECs. We also discuss chemical inhibition strategies for other undesirable microbes such as sulfate reducers and acetogens.

2. Reactor configurations

2.1. Two-chamber MECs

The concept of bioelectrohydrogenesis was first demonstrated with a two-chamber MEC design in 2005 (Liu et al., 2005). In this conventional design, the anode and cathode chambers are separated by an ion (proton) exchange membrane (Fig. 2a). Liu et al. (2005) observed that over 90% of the organic substrate (acetate) in the anode chamber was degraded at the end of batch mode with 78% coulombic efficiency (Fig. 3). However, the overall hydrogen production efficiency was only 60–73%. This is largely due to losses of the produced hydrogen in unwanted processes within the MEC, such as biomass production, conversion of substrate to polymers, and methanogenesis from hydrogen and acetate. To increase the hydrogen production efficiency in MECs, preventing hydrogen diffusion into the anode chamber is critical. Also, the internal resistance of the MEC must be minimized by reducing the distance between the electrode pair. It was reported that a higher rate of hydrogen ($1.6\ m^3\ m^{-3}\ d^{-1}$) could be obtained from two-chamber MECs using saline catholyte, which provided high solution conductivity and hence lowered ohmic resistance (Nam and Logan, 2011). The use of a membrane is considered an effective way to minimize hydrogen diffusion into the anode chamber, but it introduces complexity and cost to the process. Nonetheless, in most cases the use of two-chamber MECs only enabled hydrogen production rates ranging from 0.01 to $6.3\ m^3\ m^{-3}\ d^{-1}$(Cheng and Logan, 2011).

2.2. Single-chamber MECs

It is accepted that hydrogen evolution occurs due to the cathodic reduction reaction in MECs. The cathodic conversion efficiency (CCE) can be calculated from the ratio of e^- equivalent donated to hydrogen formation and e^- equivalent transferred from anode to cathode (Logan et al., 2008). A CCE of < 100% could be attributed to the diffusion of hydrogen to the anode surface, or to biological oxidation. It was inferred that hydrogen diffusion would decrease the CCE by up to 33% in two-chamber MECs (Tartakovsky et al., 2008). To maximize the overall efficiency of a MEC for bioelectrohydrogenesis, the e^- equivalent liberated from the anodic substrate must first be efficiently captured by the bio-anode, and subsequently dissipated at the cathode exclusively as hydrogen gas for external collection. Indeed if the produced hydrogen gas could be rapidly harvested to avoid hydrogen diffusion to the anode, the use of membrane may be omitted.

In fact, the use of single-chamber MECs for bioelectrohydrogenesis has been the subject of many earlier studies (Rozendal et al., 2007; Call and Logan, 2008; Hu et al., 2008; Tartakovsky et al., 2009). An attractive feature of single chamber MECs is that both the anode and cathode are housed within one chamber. This single chamber MEC system could be more compact with a lower capital cost. Further, single chamber MECs often exhibits a lower internal resistance. Such systems generally have low ohmic loss and concentration overpotential due to the nonexistence of detrimental pH gradient between the anolyte and

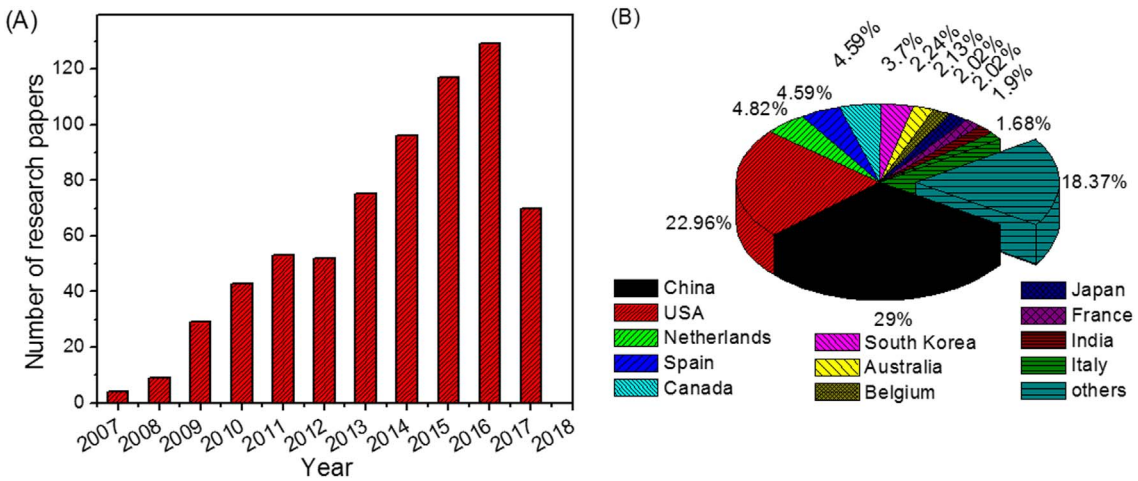

Fig. 1. (A) Year-wise publication of journal papers on MECs and (B) country wise distribution of publications on MECs. Source: "Web of Science" search with "Microbial electrolysis cell" as the research paper topic as in June 2017. (others - Saudi Arabia, Germany, Sweden, Mexico, Denmark, Taiwan, Iran, Wales, Switzerland, Malaysia, Hungary, Greece, Finland, Turkey, Singapore, Qatar, Israel, Ireland, Bulgaria, U Arab Emirates, Thailand, South Africa, Scotland, Russia, Poland, Nigeria, New Zealand, Ecuador, Austria, Vietnam, Romania, Portugal, Morocco, Lebanon, Kuwait, Indonesia, Czech Republic, Chile, Brazil, and Argentina).