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Microbial generation of H_2 or CH_4 coupled to wastewater treatment in bioelectrochemical systems

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Microbial biocathodes can be employed to produce reduced value-added compounds, such as H_2 or CH_4 in bioelectrochemical systems (BES). Here we show that selected anaerobic microbial cultures are capable of catalyzing H_2 or CH_4 production by using a carbon electrode as electron donor, via direct or indirect extracellular electron transfer mechanisms. The potential of biocathodes for gaseous biofuels production coupled to wastewater treatment in BES is discussed.

1. Introduction

1.1 Bioelectrochemical systems and extracellular electron transfer strategies

Bioelectrochemical systems (BES) are devices that employ solid electrodes to directly or indirectly stimulate microbial metabolism. Stimulation originates from the ability of some microorganisms (electro-active bacteria) to exchange electrons with solid electrodes, which accordingly serve as electron acceptors or donors in their energy metabolism (Logan, 2009) (Figure 1A). A key feature of electro-active bacteria is their ability to transport electrons outside of the cell which permits them to function in BESs. Bacteria are so far known to extracelluarly transfer (or accept) electrons to (or from) a solid surface via at least two distinct mechanisms (Figure 1B): indirect (or mediated) electron transfer and direct electron transfer.

The first relies on the redox cycling of electron shuttling compounds (also known as redox mediators) between the microorganisms and the electrodes. These electron shuttling compounds can either be naturally present redox active organic or inorganic compounds, such as humic acids and sulfur species, or are in some cases externally added or produced by the microorganisms, such as quinones or phenazines (Marsili et al., 2008). The second mechanism relies on direct contact between electroactive microorganisms and the electrode. To establish this electrochemical connection, some microorganisms utilize cythochromes or other redox active components (such as pili) located on the outer membrane (Lovley, 2008).

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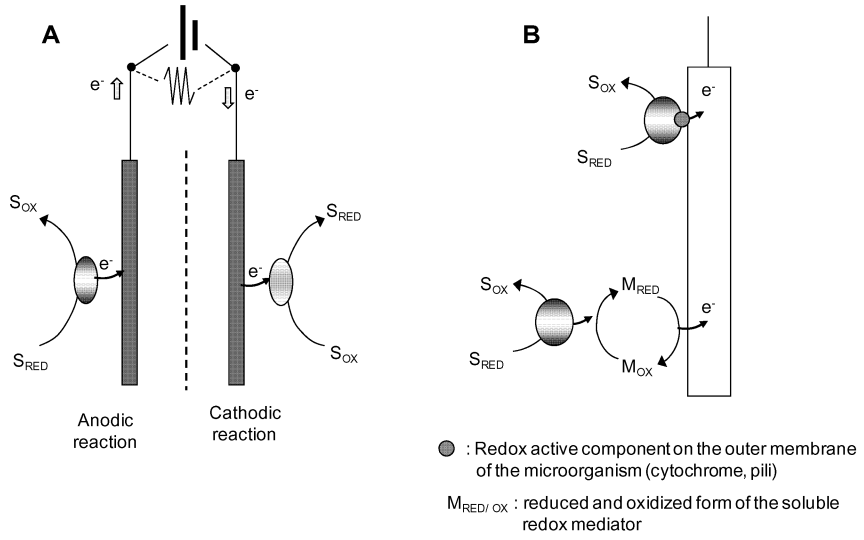

Figure 1. Interaction of microorganisms with the electrodes in a bioelectrochemical system (A); proposed extracellular electron transfer mechanisms (B).

Very recently, electro-active microorganisms have been attracting considerable attention for their potential to be used in microbial fuel cells (MFC) for the production of electricity from the oxidation of organic matter. In a MFC, bacteria use an anode as electron acceptor for the oxidation of organic carbon to CO_2, with production of protons and electrons (Figure 2A). The protons and/or other cations in solution are transferred to a cathode through a cation exchange membrane while the electrons are transferred via an electrical circuit, where a load harvests the energy liberated by the reaction. At the cathode an electron acceptor is chemically reduced using the electrons delivered by the anode. The most sustainable electron acceptor known to date for MFC is oxygen due to its availability in the environment and its high redox potential. The great interest of researchers worldwide for MFCs arises from the finding that electro-active bacteria can generate electricity from the oxidation of a large and ever-increasing number of substrates including waste materials (Aelterman et al., 2006). So far, the primary focus of MFC has been the production of electrical power coupled to wastewater treatment; however, the maximum power outputs generated thus far by these systems are quite low (10-100 W/m^3) and not yet competitive with well-established technologies for energy production such as methane fermentation (Pham et al., 2006). Alternatively, BES have been recently proposed for the production of value-added products other than electricity, such as gaseous biofuels as H_2. BES for hydrogen production are commonly referred to as microbial electrolysis cells (MEC) (Figure 2B). To produce H_2, the cathode of a BES has to be kept anaerobic; in this way the electrons released from the microbial oxidation of organic matter do not combine with oxygen to produce water (and generate electricity), but, in the presence of a suitable catalyst such as Pt or Pd, they reduce the protons to H_2.

Because substrate oxidation typically occurs at an anode potential of around ~ -0.3 V (vs SHE) and H_2 production requires a potential of -0.41 V (vs SHE, pH=7) a small

external voltage (as low as 0.11 V) needs to be added to the circuit. Notably, this voltage is substantially lower than that needed for H_2 derived from the electrolysis of water, which is typically in the range 1.8-2.0 V. Since the electron-releasing reactions (oxidation of organic waste materials) are physically separated by the electron-consuming H_2-producing reaction, this process has the potential to overcome the two major bottlenecks of the fermentative H_2 production: i.e. the need of using only carbohydrate-rich substrates and the low H_2 yields due to the accumulation of side products (acetate, butyrate …) which are not further converted into H_2.
Besides H_2, it was recently suggested that MEC could also be tuned toward the reduction of CO_2 ($E^{\circ\prime}$= -0.24 V, vs SHE, at pH=7) for CH_4 generation (Cheng et al., 2009), however, suitable catalysts for this reaction have not been found yet.

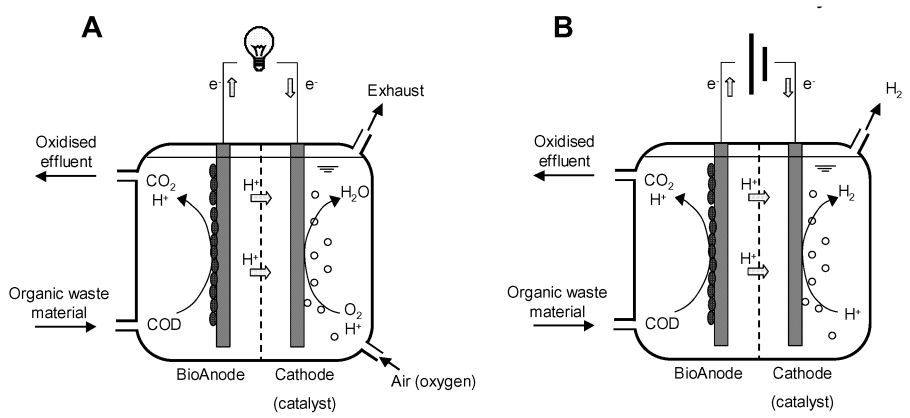

Figure 2. Schematics of a microbial fuel cell (MFC) (A) and a microbial electrolysis cell (MEC) (B).

One major limitation of MEC is related to the fact that they rely on the electrochemical reduction of protons. This reduction is typically very slow and characterized by high overpotentials, particularly at no noble metal cathodes, such as those typically employed in BES for wastewater treatment. Hence, high-rate H_2 production can be obtained only if the external voltage applied to the system is significantly higher than 0.11 V (i.e., the theoretically minimum voltage required). A groundbreaking improvement of this process would be the development of a robust, sustainable, and cheap bio-cathode which could catalyze an efficient hydrogen (or CH_4) production at high rates and low overpotentials. In the present study we describe the development and the performance of novel bio-cathodes, based on anaerobic microbial cultures, for the biological reduction of H^+ to H_2 or CO_2 to CH_4.

2. Materials and Methods

2.1 Bio-electrochemical reactor

The experiments were carried out in the cathodic chamber of lab-scale bioelectrochemical reactors, typically using a potentiostat (3-electrode configuration) to set the cathode at the desired potential. The bio-electrochemical reactor consisted of two

gastight borosilicate glass bottles (with a total volume of about 270 mL per bottle) separated by a 3 cm^2 cross-sectional area, Nafion® 117 proton exchange membrane (PEM). The cathode was a piece (50 mm x 10 mm) of carbon paper (E-TEK, working surface area ~ 8 cm^2) and the anode was a glassy carbon rod (HTW GambH, Germany; 5 mm diameter, 50 mm length, working surface area ~ 7 cm^2). The reference electrode (placed in the cathode chamber) was a KCl saturated Ag/AgCl electrode (+199 mV vs. standard hydrogen electrode, SHE) (Amel S.r.l., Milano, Italy).

2.2 The microbial cultures

Two different anaerobic cultures were investigated in this study for their ability to produce H_2 or CH_4 with a polarized cathode serving as electron donor, either in the absence or in the presence of a redox mediator. The H_2 producing culture was enriched in a fill-and-draw reactor on H_2 and trichloroethene (TCE) as electron donor and acceptor, respectively. The CH_4 producing culture was also enriched in a fill-and-draw reactor on hydrogen and bicarbonate as electron donor and acceptor, respectively.

2.3 Batch potentiostatic experiments for H_2 or CH_4 production

For the bioelectrochemical batch experiments, the cathode compartment of the bioelectrochemical cell was anaerobically filled with a H_2- or CH_4-producing culture, while the anode compartment was filled with mineral medium. Thereafter, the bioelectrochemical cell was connected to the potentiostat and the cathode potential was set at the in the range -0.65 ÷ -0.90 V (vs SHE), to evaluate the ability of microorganisms to use the negatively polarized cathode as direct electron donor for the production of methane. Methyl viologen ($E^{\circ\prime}$= -0.445 V vs. SHE) was also tested, in a range of concentrations, for its ability to accelerate the rate extracellular electron transfer process and accordingly the rate of H_2 or CH_4 production. Each test lasted 8-hours and at regular intervals gaseous samples were removed from the headspace of the compartments, using gastight syringes, and analyzed by gas-chromatography for methane and hydrogen, as described previously (Aulenta et al., 2008).

3. Results and discussion

3.1 Bioelectrochemical H_2 production

In batch experiments, H_2 was produced by the TCE-dechlorinating culture, via direct extracellular electron transfer, at cathode potentials more negative than -0.750 V vs. standard hydrogen electrode (SHE). As shown in Figure 3A, at -0.800 V vs. SHE, the rate of H_2 production in the presence of the culture was nearly 1.7 fold higher than in abiotic controls. Notably, the electrocatalytic activity of the culture was observed without preliminary acclimation in the electrochemical system. At the end of the test, the coulombic efficiency of the reaction (i.e. the fraction of consumed electrons channeled towards hydrogen production) exceeded 80%. In the presence of the soluble redox mediator methyl viologen ($E^{\circ\prime}$=-0.445 V vs. SHE), H_2 was produced by the TCE-dechlorinating culture even at much less reducing cathode potentials. Figure 3B shows the time course of H_2 production at -0.450 V vs. SHE, in the presence of 1.6 mM methyl viologen. No H_2 was produced at -0.450 V vs. SHE in abiotic controls (Figure 3B). This suggested that electrochemically reduced methyl viologen served as electron donor for

the microbially catalyzed H_2 production. Batch experiments conducted in a range of methyl viologen concentrations (0.10-3.5 mmol/L) revealed a saturation dependency of the H_2 production rate on methyl viologen concentration, with a half-velocity coefficient falling in the range of 0.5-0.6 mmol/L.

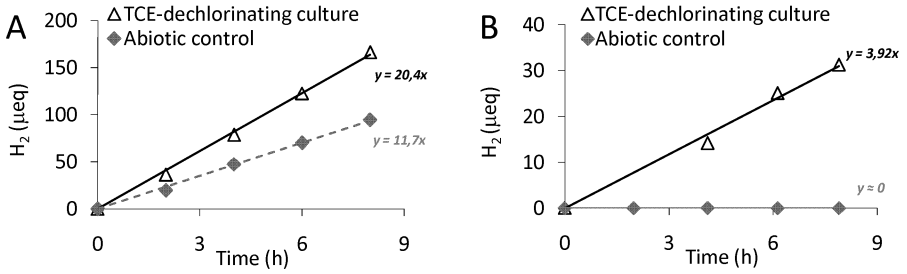

Figure 3. Time course of H_2 production in batch experiments: (A) at a cathode potential of -0.800 V vs. SHE in the absence of redox mediators; (B) at a cathode potential of -0.450 V vs. SHE, in the presence of 1.6 mM methyl viologen.

It is important to note that the maximum volumetric H_2 production rates obtained in the presence of methyl viologen were lower than those observed without mediators but at more reducing cathode potentials where, however, a major part of the produced H_2 derived from abiotic water electrolysis. Overall, the presence of the redox mediator allowed to significantly reducing the overpotentials for H_2 production.

3.2 Bioelectrochemical CH_4 production

In the absence of redox mediators, methane was produced at potentials more negative than –0.650 V vs SHE, both via direct extracellular electron transfer and via abiotically produced hydrogen gas (i.e., via hydrogenophilic methanogenesis) (Figure 4A). The relative contribution of these two mechanisms was highly dependent on the set cathode potential. Figures 4A and 4B show the results of a test carried out at -0.800 V vs. SHE in the presence or in the absence (abiotic control) of the methanogenic culture.

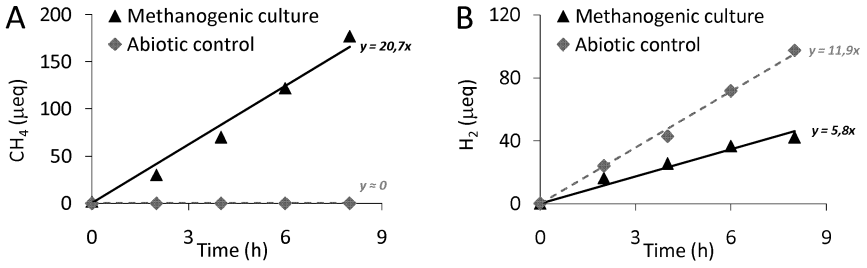

Figure 4. Time course of CH_4 (A) and H_2 (B) production in batch experiments at a cathode potential of -0.800 V vs. SHE.

Importantly, the cumulative rate of reduced end products (i.e. CH_4+H_2) formation in the presence of microorganisms was significantly higher than in the abiotic control (i.e. 26.5 vs. 11.9 μeq/h). This finding indicated that the culture enhanced the rate of electron transfer by catalyzing the formation of CH_4 also via direct extracellular electron transfer. Also in this case the coulombic efficiency exceeded 80%. Batch experiments with the methanogenic culture were also carried out at -0.450 V vs. SHE, in the presence of a range of methyl viologen concentrations. No electrocatalytic activity towards methane production was observed. Conversely, methyl viologen seemed to inhibit the activity of the methanogenic culture (data not shown).

4. Conclusions

In conclusion, this study confirmed the feasibility of producing H_2 or CH_4, at high coulombic efficiencies, using a carbon electrode as electron donor and anaerobic microbial cultures as the catalytic agents. In principle, the voltage required for cathodic H_2 or CH_4 production could be obtained, at least partially, in a MEC from the anodic biological oxidation of waste organic materials, including dilute wastewaters. Depending on applications, these reactions offer the opportunity for converting (renewable) electrical energy into gaseous biofuels.

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