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Microbial electrochemical systems for sustainable biohydrogen production: Surveying the experiences from a start-up viewpoint

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ABSTRACT

The start-up of microbial electrohydrogenesis cells (MECs) is a key-step to realize efficient biohydrogen generation and adequate, long-term operation. This review paper deals with the lessons and experiences reported on the most important aspects of H_2 producing MEC start-up. The comprehensive survey covers the assessment and discussion of the main influencing factors and methods (e.g. inocula selection, enrichment, acclimation, operating conditions and cell architecture) that assist the design of MECs. This work intends to be a helpful guide for the interested readers about the strategies employed to successfully establish microbial electrochemical cells for sustainable biohydrogen production.

1. Introduction

In the last decade, bioelectrochemical systems (BES) have become an intensively studied platform technology in various fields of biotechnological processes [1]. BES are driven by special, electrochemically-active microorganisms to achieve goals such as (i) waste treatment to serve environmental remediation [2], (ii) the production of chemicals [3] and (iii) renewable energy recovery [4]. In the last aspect, microbial fuels cells (MFC) and microbial electrohydrogenesis cells (MEC) were shown as feasible approaches [5,6]. MECs are considered to combine MFC technology with electrolysis [7]. In both MFCs and MECs, bacteria work under anaerobic conditions at an anode to oxidize various substrates ranging from simple compounds i.e. sugars, organic acids [8] to complex organic matter including wastewaters of distinct origin [9–11] as well as fermentation effluents [12]. As a results, either bioelectric potential (in MFC) or H_2 gas (in MEC) is obtained. It was lately argued based on life-cycle assessment that the conversion of organic feedstock to bioH_2 in MECs is a highly attractive way to go from an environmental protection standpoint [13,14], which suggests the potential contribution of this technology to sustainability.

In principles, MECs apply two electrodes (the anode and the cathode) under anaerobic circumstances [15]. The anode is the important place for exoelectrogenic strains that after colonizing its surface, form an anode-respiring biofilm. In essence, attributed to the metabolic activity of the biofilm, electrons and protons are released from successful substrate conversion/degradation. The electrons are transferred to the anode (as final electron acceptor) by different possible mechanisms (discussed later) and pass subsequently to the cathode via an external circuit. At the cathode, which plays the role of an electron donor, the reduction of H^+ to molecular H_2 gas takes place. Unfortunately, this phenomena is non-spontaneous (thermodynamically not favored due to the positive Gibbs free-energy of the reaction) and therefore an external voltage, practically at least 0.2–0.25 V must be supplemented to make it happen (Fig. 1). The consecutive reactions (anodic substrate degradation and cathodic product (H_2) formation) can be either done in single- or two-chambered arrangement. In the latter case, the anode and cathode are spatially separated, in general by a membrane possessing ion-exchange capacity.

Basically, the achievable, steady-state performance of MECs depends strongly on the way it is started-up, which is known as a crucial step for H_2 producing biotechnological systems [16]. The start-up could have a great importance to maximize the H_2 production capacity of the MEC and should involve the establishment of efficient and robust biofilms [17–19]. To achieve adequate start-up, the source of inocula

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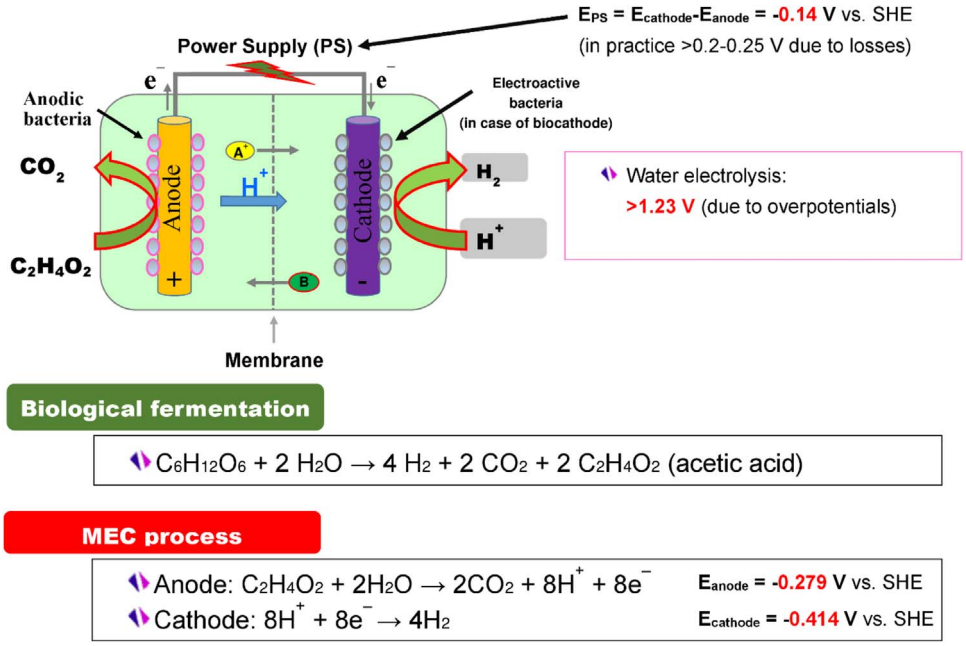

Fig. 1. Principles of H_2 production in microbial electrolysis cell.

(containing the exoelectrogenic strains), consequent enrichment and acclimation methods to select bacteria with high bioelectrochmical activity seem to be of high concern since the characteristics of the anode-surface grown biofilm (i.e. its composition and state) determine the attractiveness of BES [20–23]. In addition to these biotic factors, the start-up process ought to deal with the operating conditions (such as anodic potential, temperature, substrate and its concentration) and the cell architecture so as to positively influence the biofilm development and optimize the MEC from the point of view of H_2 production rate/yield and other (energetic) process indicators e.g. Coulombic-efficiency, cathodic H_2 recovery, current density, etc. However, even though the start-up is a key-element for longer-term MEC viability [24], to our knowledge, no comprehensive article has been specifically dedicated to overview and assess the lessons and experiences gained in this field. Since MECs can be viewed as MFC-derived technologies with significant modifications on the cathode side, the start-up methods could reflect quite a number of similarities, especially related to the bioanode development [20]. Hence, in this paper, it was aimed to review the most essential factors and design considerations related to MEC start-up and give an insight to the progress how the recent accomplishments have improved the methodological approaches and enriched the international knowledge in this field.

2. Effects of start-up variables on MEC performance

2.1. Inoculum for MEC start-up

INOCULA containing anode-respiring bacteria can be delivered from various environments [25,26] and dozens of strains were found to have sufficient capability for powering BES via biocurrent generation by (i) exocellular electron transfer relying either on membrane cytochromes, (ii) artificial/self-secreted mediators or (iii) electro-conductive appendages [27–29]. To select the microbial species (with appropriate electrochemical activity) to be used in biological fuel cells, a fast screening method was lately reported by Szöllősi et al. [30].

BES can apply both pure- and mixed cultures for inoculation. The use of pure isolates in bioelectrochemical applications could be important to conduct fundamental studies and to gain a better understanding about strain characteristics, behavior and functionalities (i.e. electron-transfer mechanism of the particular bacteria) [21]. Moreover, single-strains can be employed in the frame of bioaugmentation concept in order to reinforce mixed populations and obtain a better microbial equilibrium, which, in turn, leads to a higher capacity, exoelectrogenic biofilms and improved operational stability [20,31]. Systematic investigation and deeper comprehension on community ecology e.g. revealing the interactions in the fixed anodic-biofilms could be a valuable tool to enhance BES performance [22,32]. For instance, the syntrophy of anode-respiring bacteria with fermenting microorganisms seems to be advantageous [33] since the members of the latter class are able to efficiently decompose complex organic matter to simple compounds such as acetate, which represent easily biodegradable substrates for the former group.

Although pure culture BESs fit perfectly for principle studies, practical one should rely on mixed cultures. As concluded in the review by Liu et al. [27], these communities, in most cases, generate higher currents and provide better stability in comparison with single-strain systems. The further advantage of such communities could be the potential versatility and flexibility that are required for real-case, non-sterile applications. These could be good reasons behind the fact that microbial consortia appear to be more feasible to inoculate BES. Nevertheless, depending on the source of mixed inoculum, the reactor start-up and concomitant operational behavior e.g. in terms of process lag-phase can be significantly different [34]. Hence, to increase the probability of appropriate start-up and fair performance in longer-terms, techniques can be proposed for mixed culture microbial electrochemical cells that may result in an enriched consortia with better properties.

These enrichment methods (being either electrochemical or chemical) make it possible targeting specific groups of efficient exoelectrogenic species such as *Geobacteraceae* [35–37]. This preliminary selection, controlled growth and acclimation of biocatalysts could have substantial practical advantage since besides the physiological state of the bacterial cells [38,39], the profile of the active microbial community developing on the anode during the start-up period is a factor that directly affects the MEC operation [40,41]. For instance, Boghani et al. [42] underlined that an optimized, electrochemical-strategy can be applicable to control biofilm enrichment, cut the start-up time demand and increase the capacity of the bioelectrochemical cell. Interestingly, Borjas et al. [38] demonstrated a 20-fold faster start-up period and a concurrent, 6-fold enhancement of COD removal during continuous