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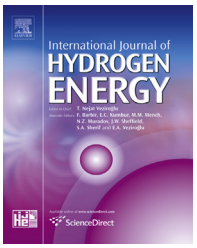

Enrichment strategy for enhanced bioelectrochemical hydrogen production and the prevention of methanogenesis

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ABSTRACT

The influence of acetate and butyrate enrichment on biofilm structure for enhanced electricity and hydrogen production was investigated using bioelectrochemical systems (BES). Two reactors were enriched for 9 weeks using 20 mM L^{-1} acetate (AC) and butyrate (BU) in microbial fuel cell mode before transfer into MECs. Acetate and butyrate (20, 10 and 5 mM L^{-1}) substrates were sequentially used as feedstocks for the AC and BU acclimated reactors. Both BU and AC reactors gave initial hydrogen production rates of 200 ± 50 cm^3_{STP}/L_{anode}/day with a H_2 yield of 0.585 ± 0.085 mol mol^{-1} but when the substrates were switched, the BU (MEC) hydrogen production rate increased to 249 ± 3.0 cm^3_{STP}/L_{anode}/day and the AC (MEC) decreased to 0 cm^3_{STP}/L_{anode}/day. It was demonstrated that the amount of methane produced by MEC (BU) was 58 ± 5% lower than that produced by MEC (AC). These results show that butyrate fed BES on an equivalent molar basis, improved MEC bioanodic performance and demonstrated the potential to improve overall performance of an integrated hydrogen fermentation and BES system.

Introduction

Rising concern about emissions from the consumption of fossil fuels being linked to the climate change along with the need for sustainable organic waste treatment have directed considerable research towards alternative fuels. One promising renewable technology that has gained wide interest in the past decade are reactors based on bio-electrochemical systems (BESs). These reactors are able to recover electricity and hydrogen from what otherwise would be waste products [1,2]. BES have been studied as alternatives to conventional wastewater treatment as they have the potential to reduce the energy demand from oxygenation as part of activated sludge processes [3,4], while supporting sustainable electricity

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generation. A recent focus of this work has been on strategies to enable the scale-up of this technology [5].

BES consists of an anode, cathode and a separation membrane. These systems are may be operated as microbial fuel cells (MFC), in which they deliver electrical power, or as microbial electrolysis cells (MEC), in which the electrical reducing power is applied to drive a thermodynamically unfavorable reaction [6]. The electricity production in MFCs is achieved by exoelectrogens, microorganisms capable of exocellular electron transfer, consequently these systems are capable of processing a wide range of biomass/wastewaters [7]. The electrons are conveyed to the anode surface and then from anode to cathode, where the protons delivered in a counter current are oxidized to water in an oxygen reduction reaction. MECs have a similar architecture to MFCs but the cathodic reaction involves the reduction of protons to hydrogen in an anaerobic compartment, thus MECs are able to produce hydrogen whilst also removing organic contaminants from the wastewater. Microbial electrolysis can thus be seen as a biological analogue of chemical electrolysis, which theoretically requires the input of ca. 0.115 V, for 20 mM acetate and 0.052 V, for 20 mM butyrate solution, instead of 1.2 V, needed for equivalent conventional water electrolysis. In practice, however, voltages of 0.5–0.85 V are typically applied to overcome the voltage deficit from bioelectrogenesis and electrode overpotential and other losses [8].

Since hydrogen is widely proposed to be a significant future energy vector, there is a requirement to develop sustainable processes that are able to reduce the energy required during its production when using traditional technologies, particularly as demand will likely increase over time [9,10].

A current area of research is focused on the use of BES to process the effluents from two stage hydrogen fermentation systems [11], in order to facilitate increased hydrogen yields. Low hydrogen yields of 2–4 mol H_2 mol^{-1} of glucose are typically observed when acetate and butyrate are the main products of the fermentation, giving typical overall yields of 16–33% when compared to the theoretical maximum of 12 mol mol^{-1} [12], as indicated by Eqs. (1)–(3).

$$C_6H_{12}O_2 + 2H_2O \rightarrow 2C_2H_4O_2 + 4H_2 + 2CO_2 \quad (1)$$

$$C_6H_{12}O_2 + 2H_2O \rightarrow 2C_4H_8O_2 + 2H_2 + 2CO_2 \quad (2)$$

$$C_6H_{12}O_2 + 6H_2O \rightarrow 12H_2 + 6CO_2 \quad (3)$$

It is theoretically possible to produce 4 mol H_2 mol^{-1} of acetate and 8 mol H_2 mol^{-1} of butyrate if a two-step process is considered; or with butyrate as the sole substrate 10 mol H_2 mol^{-1} of butyrate (shown below). Previous studies have investigated the use of small scale reactors systems to convert the effluent from hydrogen fermentation into hydrogen, these processes produced yields of 3.65 mol H_2 mol^{-1} of acetate and 2 mol H_2 mol^{-1} of butyrate [13,14].

$$\text{Anode: } C_4H_8O_2 + 2H_2O \rightarrow 2C_2H_4O_2 + 4H^+ + 4e^- \quad (4)$$

$$\text{Cathode: } 4H^+ + 4e^- \rightarrow 2H_2 \quad (5)$$

$$\text{Anode: } C_2H_4O_2 + 2H_2O \rightarrow 8H^+ + 8e^- + 2CO_2 \quad (6)$$

$$\text{Cathode: } 8H^+ + 8e^- \rightarrow 4H_2 \quad (7)$$

However limited research has been carried out on the integration of hydrogen fermentation and MEC systems to maximize the theoretical production yields of biohydrogen [15].

This work aims to enhance bio-anode performance by improving the electrode configuration and exploring how different concentrations of butyrate in the acetate/butyrate mixture affect the hydrogen and methane production rates. Whilst development of cathode performance often entails the use of expensive catalysts or the manufacture of specialist cathode materials [16], anode biocatalytic performance can be often improved using strategies such as increasing surface area and biofilm acclimation [17,18].

Acetate and butyrate mixtures are common by-products of hydrogen fermentation but the proportions of these VFAs will vary depending on operating conditions [19], e.g. the product ratios from hydrogen fermentations have been reported as 60% butyrate and 40% acetate and 90% butyrate and 10% acetate mixtures [20,21]. It is important to assess how MEC anodic biofilms acclimated to pure acetate or butyrate respond to these changes in acetate and butyrate proportions in the mixture, as is the is the effect of acclimation on Archeal population development and rates of methanogenesis as this can have significant effects of process efficacy. A carbon veil spirally rolled anode design around a conductive carbon rod was used to provide a large surface area for bacterial adhesion, as well as ensuring efficient current collection. The cost of these materials is significantly lower than carbon foam and carbon mesh anodes [22,23], which makes these anodes more suitable for the large scale application.

The effect of substrate type and concentration on the performance of concentric continuous flow reactors was assessed for operation with fermentation volatile fatty acid products. To the author's knowledge no previous studies have been carried using a range of different concentrations of acetate and butyrate and acetate/butyrate mixtures to investigate the effect of substrate enrichment on preventing methanogenesis and improving hydrogen production and system performance using a scalable MEC system.

Materials and methods

Electrode and MFC assembly

Each MFC consisted of one cell constructed from a 40 mm ID tubular opaque polypropylene. The tube (200 cm^3 volume) was radially perforated (53 holes each 10 mm in diameter) on one side of the tube. Each tubular cell was assembled around a carbon anode, 17.2 mm OD, 200 mm tall and each anode was

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